AN INTRODUCTION TO THE STUDY OF METALLOGRAPHY AND MACROGRAPHY

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BY

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INGÉNIEUR DES ARTS ET MANUFACTURES CHEF DES TRAVAUX DE MÉTALLURGIE ET DE MÉTALLOGRAPHIE A L'ÉCOLE CENTRALE DES ARTS ET MANUFACTURES

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INTRODUCTION TO THE ENGLISH EDITION

By H. C. H. CARPENTER, F.R.S.,

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DURING the last fifteen years a number of text-books on Metallography have been published in the English language. Amongst those of a general character may be mentioned the books by Law, Desch, Gulliver, and Rosenhain, while in regard to the metallography of iron and steel the text-books of Sauveur, Howe, and Edwards fill an important place. It might be considered, therefore, that the literature on the subject was sufficient for the present. Metallography, however, is still a young and rapidly growing science, and it seemed to the writer that there is room for a book which will present in English some of the characteristic features of French work on this subject. The desirability of this will be generally admitted when it is remembered what an important part the contributions of the late Monsieur Osmond, Professor Henri Le Chatelier, Messrs. Charpy, Guillet, and others have made to the foundation and development of this science.

The publication of a translation of the book by Messrs. Guillet and Portevin, entitled "An Introduction to the Study of Metallography and Macrography," is to be welcomed, in the first place, because the authors are themselves distinguished original investigators in the subject and therefore write with a first-hand knowledge and command of it. Evidence of this is furnished by the numerous excellent photographic illustrations which are largely taken from their own papers. Each of them occupied for several years an important technical position in the French metallurgical industry, and is accordingly well acquainted with its practical requirements. In the next place, the book is a characteristically French product and presents a view of the subject which is not quite the same as that of any of the books already alluded to. A still more important reason for welcoming it lies in its broad title, in which it is to be noted that the two words Metallography and Macrography are included. As the authors point out, the latter is really the older science and dates from the work of Widmanstaetten, first published in 1808. He it was who first conceived the idea of coarsely polishing

metallic surfaces and afterwards etching and examining them. Macrography may be defined as the study of the "coarse" structure of any given metal or alloy. It does not require expensive or complicated microscopic apparatus. It is a curious thing that in spite of this there should have been a much more rapid development of the science of metallography which definitely relates to the microscopic structure of the metal and requires for its execution the use of comparatively expensive apparatus such as microscopes with high resolving objectives, pyrometers, etc.

Metallography as a science can scarcely be said to date from earlier than 1894, when the late Monsieur Osmond published his remarkable memoir on the Constituents of Carbon Steels. It was this paper more than any other which gave the impetus to the astonishing development of metallography both as a pure and an applied science, which has continued down to the present day. There was, however, especially in the investigation of metal failures, a tendency to draw conclusions from microstructures which were based upon the examination of a comparatively small area without taking sufficiently into account the possibility that the metal in question was by no means necessarily homogeneous. Accordingly in recent years it has become recognised that a careful study of the macro-structure of a metal in so far as it can be revealed by quite simple methods of grinding, etching, examination with a hand lens, taking of prints, etc., should be undertaken before an investigation of its microstructure is made. It is recognised now that in all such investigations macrography must precede metallography, otherwise quite erroneous conclusions are liable to be drawn.

The aim of the book has been, to use the authors' words, "to outline principles and to illustrate them by means of the most typical and important examples." It is therefore intended as an introduction to the study of the subject. Undoubtedly, however, its general purpose is practical, and it should be not merely of service to those desiring to gain some insight into the science, but also of real assistance to those engaged whether in manufacturing or using metals. Only sufficient theory is introduced to enable the behaviour of metals and alloys under these conditions to be rendered intelligible. A feature of especial value in the Metallographical section is the discussion in Chapter III of the relation between equilibrium diagrams of alloys and their properties and correct mechanical treatment. It is important that this task should have been undertaken, for it has a vital bearing on the application of metallographical theory to everyday works practice, and in no book with which the writer is acquainted has the attempt been more successfully carried through. Attention may further be drawn to Chapters VI and VII, dealing respectively with the technique of macrography and its industrial applications, which set forth very compactly the numerous ways in which the results given by this method

can be made to build up the story of the changes through which the metal reaches its form in any given case.

The translation has been undertaken by Mr. Leonard Taverner, A.R.S.M., D.I.C., who is in charge of the Metallographic Department of the Royal School of Mines. It is an excellent piece of work, which has done, I think, full justice to the original French.

H. C. H. CARPENTER.

September 20th, 1921.

TRANSLATOR'S FOREWORD

THE work of Professors Guillet and Portevin needs no introduction to English-speaking metallurgists; but it is hoped that the present translation will render it more accessible as a text-book and work of reference. The authors have considered both the theoretical and practical sides of the question, and although emphasising the necessity of a theoretical basis of study, they have not overlooked the fact that the ultimate aim of such study lies in its practical application to industry. The book, therefore, should make a strong appeal to both the practical engineer and the student. Apology is due for the French phrasing to be found in many parts; but as it is a descriptive technical work this was considered essential in order to retain the exact meaning, particular care having been taken in translation to maintain the character of the original.

Amongst the special features of the book may be mentioned the detailed description of the constituents and structures of carbon steels and the relatively complete account of the special or alloy steels, to which subject the authors have contributed much valuable research. The impurities of the ordinary industrial metals are dealt with at some length, and wherever possible the relation between the microscopical structure and the mechanical properties and treatment is brought into prominence. The final section of the book is devoted to the methods of macrographical examination of both ferrous and non-ferrous material, and should constitute a very valuable addition to the literature on the subject, since the French have recently given considerable attention to this type of investigation.

The very complete collection of plates relative to the text renders the book of great value to the student, and the addition of an index to the English edition should aid the reader materially in cases of reference.

L. T.

LONDON,
September, 1921.

PREFACE

THE title, "An Introduction to the Study of Metallography and Macrography," clearly indicates the purpose of this book. The reader should not expect to find, in this little volume, descriptions of all types of apparatus in use, or records of the enormous amount of metallographic work that has been carried out during the last fifteen years; likewise, references are only quoted when the reader is recommended to consult other works for further information, not within the scope of the present volume.

The aim has been to outline principles and to illustrate them by means of the most typical and important industrial examples. The book is therefore intended as an introduction to the study of Metallography. It is based on the course of instruction given jointly by the authors at the École Centrale des Arts et Manufactures, and continued by one of the authors at the Conservatoire National des Arts et Métiers. Ultimately the authors hope to deal fully with the subject of this work in their "Traite de Metallographie" to be published at a later date.

INTRODUCTION

METALLOGRAPHY may be defined as the microscopical study of polished and etched metallurgical specimens.

The examination is carried out not by transmitted light as in the case of many histological and petrological specimens, but by reflected light; one face of the metal specimen is perfectly polished, then etched by a suitable reagent having a differential effect on the various constituents, and finally examined under the microscope at varying magnifications up to, and in special instances exceeding, one thousand diameters. Macrography may be defined as the study of coarsely polished and etched metallurgical specimens without the aid of a microscope. It is especially useful in the detection of certain qualities or defects, and also enables a general estimation of the constitution of the material to be made.

Owing to metallography being essentially based on the physico-chemical laws, it has been considered desirable to describe, as briefly as possible, the equilibrium diagram and to illustrate its relation with the structure and principal physical and mechanical properties of an alloy. Further, one of the most important industrial questions being the direct relationship which exists between the constitution of metallurgical products, their properties and their treatment (mechanical, heat, or chemical) several pages have been devoted to a brief outline of these points.

Before commencing any description of the two subjects to be considered, it appears desirable, in the first place, to give a concise summary of their history.

Widmanstaetten, in 1808, was the first to conceive the idea of coarsely polishing metallic surfaces in order to examine them after etching, and thus arose the study of Macrographic Structure, in which work such great advances have recently been made by Frémont and de Heyn. The first microscopical examination of metallurgical specimens appears to have been due to the Russian General Anossow, while Sorby, who founded the science of Petrology in 1856, applied the method of examination by reflected light after etching, to meteorites and certain metallurgical products (1864). Some years later, Martens examined, very briefly, numerous samples of cast iron

and steel. Until 1883 no further development occurred ; for, although the method of investigation was established, the previous work had aroused but little interest.

At this date (July, 1883), two Frenchmen—Osmond and Werth, engineers attached to the works of Schneider and Creusot—published "La Théorie Cellulaire des Aciers," in which they showed that steel consisted of a core of iron surrounded by a cement which disappeared on quenching, *i.e.* heating to a high temperature followed by rapid cooling in water. Again in 1894, in the *Bulletin de la Société d'Encouragement pour l'Industrie nationale*, Osmond published his memoir of epoch-making importance, on the constitution of carbon steels, a memoir accompanied by many excellent photo-micrographs to which recent research has added but little. This work aroused considerable interest ; research was started in every direction, the technique became simpler as experience progressed, the microscope from being merely an instrument of the scientific laboratory commenced to become an indispensable instrument in metallurgical and engineering works.

With the more recent researches are associated the names of Henry Le Chatelier and his numerous pupils, Osmond, Cartaud and Charpy, in France ; in Russia, Tschernoff, Baykoff, Belaïew ; in Germany, Martens, Heyn and Bauer, Wüst, Goerens, Tammann, Guertler and Friedrich ; in England, Roberts-Austen, Stead, Arnold, Carpenter, Ewing and Rosenhain ; in the United States, Howe, Sauveur, Campbell, Bancroft ; in Holland, Behrens ; in Denmark, Hannover ; in Sweden, Bénédicks ; in Italy, Giolliti and his pupils.

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PART I

METALLOGRAPHY

CHAPTER I

METHODS OF INVESTIGATION

METALLOGRAPHY consists, as previously mentioned, in the examination of a polished and etched surface of a metal by reflected light.

Such an examination may be divided into four principal operations :

(1) Selection of the specimen.

(2) Polishing.

(3) Etching.

(4) Microscopical examination, and photographic record when required.

1. SELECTION OF THE SPECIMEN

This operation will be considered under three headings :

1. The position from which the specimen is to be obtained.

2. The method and necessary precautions to be taken in obtaining the specimen.

3. The state or condition of the metal from which the specimen is to be taken : viz. hardened, annealed, etc.

1. The position from which the specimen is taken is of primary importance, and depends largely on the purpose of the examination. If the general structure of an article has to be examined, and it can be cut up, samples may be taken from the centre and each end.

Frequently the article is required for further use, in which case the positions from which specimens can be taken are limited.

In the case of a failure during use, a fracture for example, the fracture itself should be microscopically examined. Specimens of this character require the greatest care in polishing to ensure that the fractured edge is not destroyed.[1]

There is another method of investigation—macrographic examination—to be fully explained later, that gives great assistance in the

[1] Rosenhain's method may be advantageously used in the investigation of fractures. The article to be examined is first electro-plated with copper. The copper protects the fracture during the subsequent cutting and polishing operations.

selection of a specimen. Macrographic examination shows quite clearly the homogeneous areas, heterogeneous areas (segregation and liquation), and, in many instances, the flow lines of the metal.

Attention must also be given to the orientation of the specimen with regard to the direction of forging or rolling.

Finally, the exact position from which the specimen is taken must be noted and the back of the specimen marked so that the relative position of the polished face is known.

The two photographs (Pl. I., Figs. 1 and 2) of puddled iron are typical examples. Fig. 1 shows a section in the direction of forging: the slag is elongated in one direction by the mechanical treatment; Fig. 2 shows a section at right angles to the direction of rolling: the slag fibres have been cut through in the plane of the polished face. Pl. I., Figs. 3 and 4, illustrate the effects of rolling in the case of an annealed medium carbon steel.

2. The specimen is usually obtained by cutting off a small portion with a hack-saw. When the material is very hard it is easier and less costly to use a thin carborundum wheel. Care is required when thin carborundum wheels are used, as any angular movement of the article being cut will fracture the wheel. If the material is very brittle (ferro-alloys, bronzes rich in tin, etc.) it can be fractured with a hammer and a suitable piece selected for grinding and polishing.

3. The material from which the specimen is to be obtained may have been cast, rolled, forged, stamped, drawn, annealed, quenched, etc.

The treatment that the metal has undergone is of the utmost importance, and must be clearly defined when considering the microscopical structure. These questions will be fully dealt with in Chap. IV. under the heading of "The Industrial Applications of Metallography." However, in most cases, the material is examined either in the condition in which it is delivered or else after some special treatment preparatory to use, such as annealing.

The dimensions of the specimens vary considerably. Certain microscopes are so constructed that relatively large areas can be examined without any great inconvenience, but in most cases it is advisable to limit the size of the specimen to approximately 10 mm. × 10 mm. × 8 mm. thick.

When necessary much smaller specimens (1–2 mm. sq.) can be examined. In such cases it is usual to embed the specimen in fusible metal, solder, sealing-wax, or other suitable medium, by which means the finest wire, turnings, and even filings may be examined.

TYPICAL STRUCTURES OF DIFFERENT SECTIONS OF THE SAME SPECIMEN.

1° Wrought iron showing slag inclusions (unetched).

(× 57.)

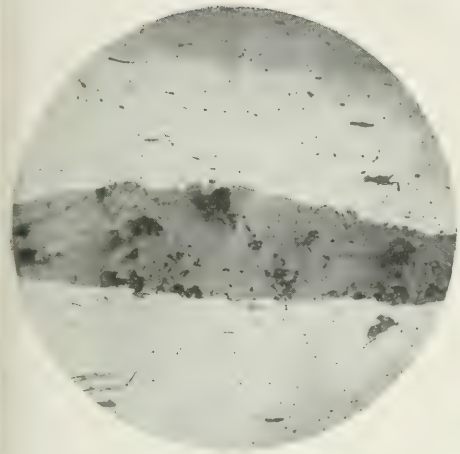


FIG. 1.—Section in the direction of forging.

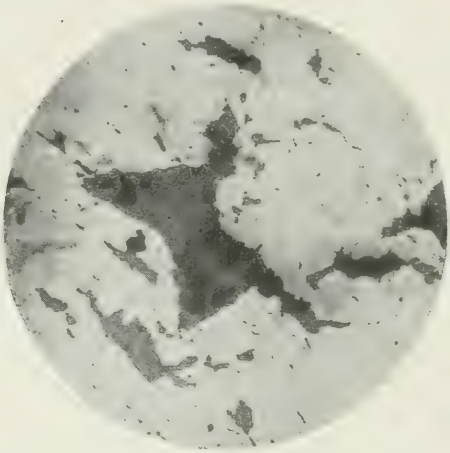


FIG. 2.—Section at right angles to direction of forging.

2° Medium carbon steel, annealed.

(C = 0·3 %; Mn = 0·34 %; Si = 0·19; S = 0·056; P = 0·061.) Etchant: Bénédicks' reagent.

(× 200.)

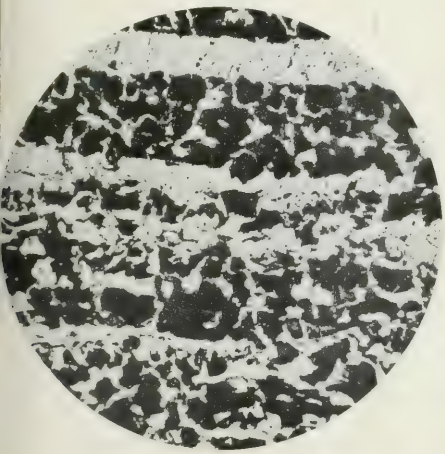


FIG. 3.—Section in the direction of rolling.

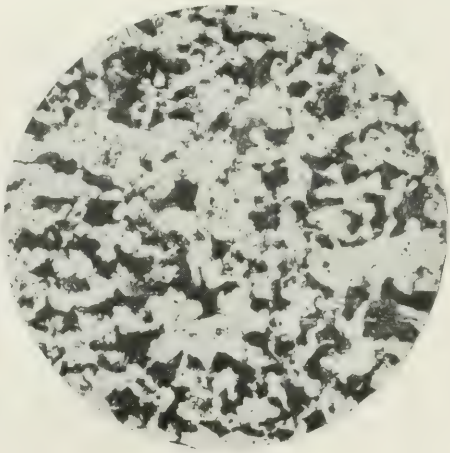


FIG. 4.—Section at right angles to direction of rolling.

PREPARATION OF SPECIMEN.

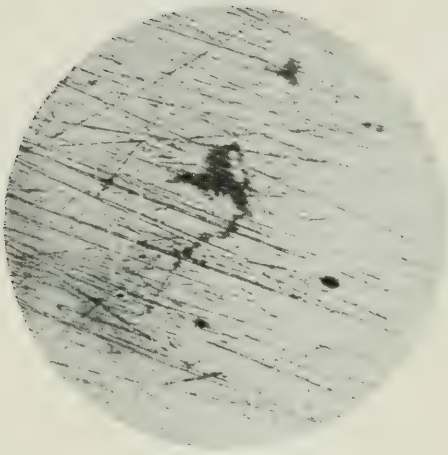


FIG. 18.—The specimen partially polished.
The slag is seen through the scratches.

FIG. 19.—Polished specimen unetched.
The slag is clearly seen.

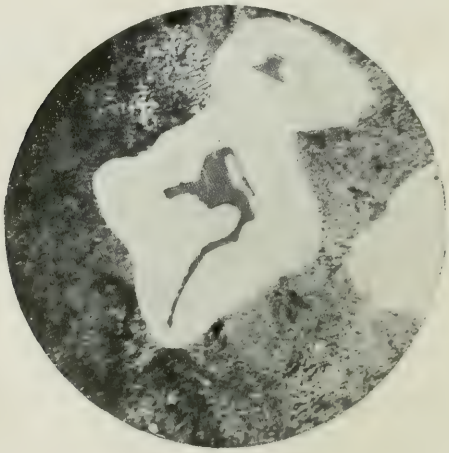


FIG. 20.—The specimen after etching.
The slag is shown in the same position in the centre of the white area.

2. POLISHING

For many years the polishing of a metal specimen for microscopical examination was considered an operation requiring the greatest skill. New methods, introduced by Le Chatelier, have greatly simplified this operation, and excellent results may now be obtained if a few simple precautions are observed.

Polishing is carried out in three stages :—

(A) Grinding or filing to obtain a flat surface.

(B) Fine grinding on emery papers.

(C) Wet polishing, which gives the desired polish and leaves no trace of scratches. It must be remembered that magnifications of 500 to 1000 diameters are used in the examination of many specimens.

(A) **Grinding.**—The object of filing or grinding is to form a flat surface on the specimen obtained from the hack-saw or by fracture. An emery or carborundum wheel is usually used for this purpose. These wheels are mounted either vertically or horizontally and run at speeds from 1500–4000 r.p.m., depending on the texture and diameter of the wheels. Various means are used to drive the wheels : foot-power, shafting, etc. ; a convenient method being to mount the wheel direct on a variable speed motor. It is always advisable to have a slide-rest, close to the wheel, against which the specimen may be held.

When the wheels are mounted vertically, the one spindle usually carries two or sometimes four wheels. In the case to be considered only two wheels are used ; a carborundum wheel to obtain a flat surface, and a disc which has been surfaced with coarse emery paper ; the purpose of this disc is to lessen the work and time required for fine grinding.

The softer metals may be more easily and better dealt with by filing, and should not be ground on the wheels.

When the edge of the specimen is not required for examination it is advisable to file or grind off the edges and corners and thereby lessen the danger of tearing the emery papers and polishing cloths used in the later operations.

Precautions must be taken to avoid any heating of the specimen both in sawing off and in the subsequent polishing operations. A rise in temperature of 100°–200° C. would have a great effect on certain metals, notably quenched or cold-worked alloys. This may be avoided by keeping the specimen continuously moistened, or by frequent quenching in water, during the polishing operations. The temperature of the back of the specimen is no criterion of the temperature of the face of the specimen which alone is of consequence. The specimen should never feel warm to the hand, for this would signify a considerable rise in temperature of the face being ground.

The mounting of specimens too small to handle may be carried out by inserting them in steel or brass tubes, which are then filled with sealing wax or other suitable material. The specimen should first be ground as flat as possible, after which it is placed face downwards on a glass plate or other flat surface and, the brass tube having been placed over the top of the specimen, the melted wax is poured in. Finally, the tube and wax are heated by a bunsen burner to allow the wax to flow freely and fill up any cavities.

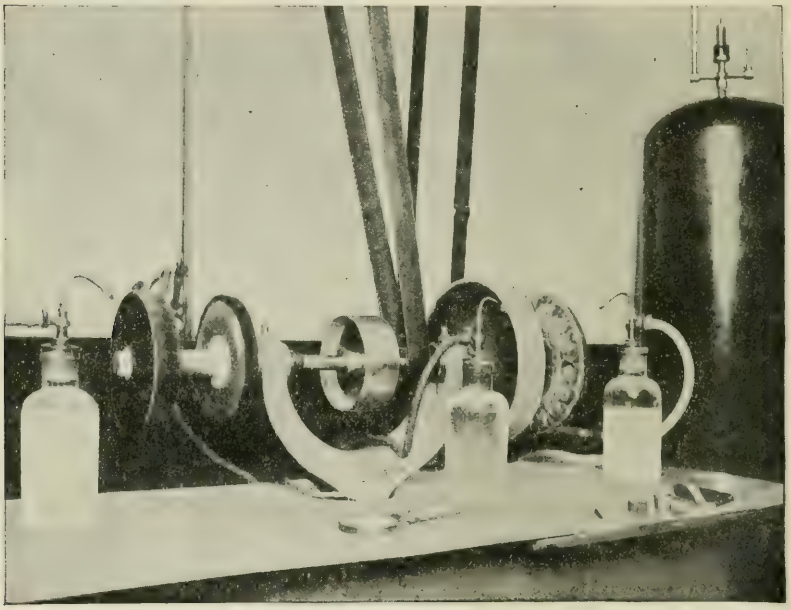


Fig. 5.—Vertical polishing machine fitted with four discs (alumina-water sprays in front of the discs).

(B) **Fine Grinding.**—The second and longest operation forms a surface on the specimen, consisting of a series of very fine scratches, which may be easily and quickly removed by wet polishing. The operation is carried out on a series of surfaces previously dressed with abrasives of different grades. The specimen is held so that the scratches from the abrasive will be formed in one direction only, and the rubbing down is continued until all other scratches are removed.

The specimen is then transferred to the next finer abrasive. It is turned through an angle of 90° and the rubbing down continued until the scratches from the previous paper are entirely eliminated. The specimen now passes to the next finer paper and the operation is repeated. Finally, the specimen leaves the last paper with a series of scratches entirely formed by the finest abrasive used. The

surface of the metal consists of a very thin strained layer, which, according to Osmond and Cartaud, is of varying thickness, depending on the grade of emery used (*Revue générale des Sciences*, **16**, 57, 1905). For many years it was believed that different materials required different grades of polishing powders or abrasives. In practice, the same two grades of abrasives are used for all metals: emery paper 0000, emery powder 0000.

There are many methods of using the various polishing and grinding materials: emery papers fixed on revolving discs (Martens); cloths tightly stretched on boards and then dressed with emery powder (Chatelier); both of these methods having the disadvantage that it is necessary to have at least as many discs or boards as grades of emery. The simplest and best method is to rub down the specimen by hand on a piece of emery paper placed on any flat surface, such as a glass plate, care being taken that no dirt, etc., is under the paper. The French emery papers (Hubert) will be found quite satisfactory for this purpose. Grades 1, 0, 00, 000, 0000.[1]

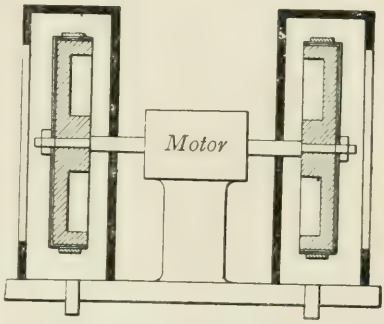


FIG. 6.—Enclosed vertical grinding-discs with direct motor-drive (Goerens).

(C) **Polishing.**—The operation of polishing a metal specimen for microscopical examination may be easily performed with the modern appliances if certain precautions are taken in the preparation and care of the polishing powders and wheels. The polishing wheels must be made of material impervious to water, usually metal (brass), but well seasoned hard wood may be substituted if the working face is protected by a covering of sheet metal (zinc). The polishing cloth is stretched tightly over the wheel and fastened at the sides or back by means of a spring or other suitable device. Care is required in the selection of a suitable cloth, which must be thick, soft, smooth, and free from any hard material.[2] Before use it is advisable to wash the cloths with soap and ammonia to remove all traces of grease, grit, etc. To obtain satisfactory results, the wheels should be run at speeds varying from 1000–1800 r.p.m. They may be mounted vertically or horizontally, in the former case the usual practice being to mount two or four wheels on one shaft. Some protection from dust must be provided; the most satisfactory arrangement consisting of a complete metal covering with a detachable lid, which

[1] It is frequently possible to omit papers 000, 0000, and pass direct from the 00 paper to the coarse wet polishing wheel.—Trans.

[2] Discs of fine compressed felt are sometimes employed for the harder alloys.

is removed when the polishing cloth is required for use. A specially designed room (enamelled walls, oiled floor, etc.) is frequently reserved for polishing operations in large laboratories, to ensure that the polishing machines may be completely isolated from dust, etc. Although the above-mentioned precautions are essential the perfection of the final polish will depend mainly on the quality of the polishing powder.

The preparation of satisfactory polishing powders has been greatly facilitated by new methods introduced by Le Chatelier, the direct result of which has been the simplification of the operation of polishing.

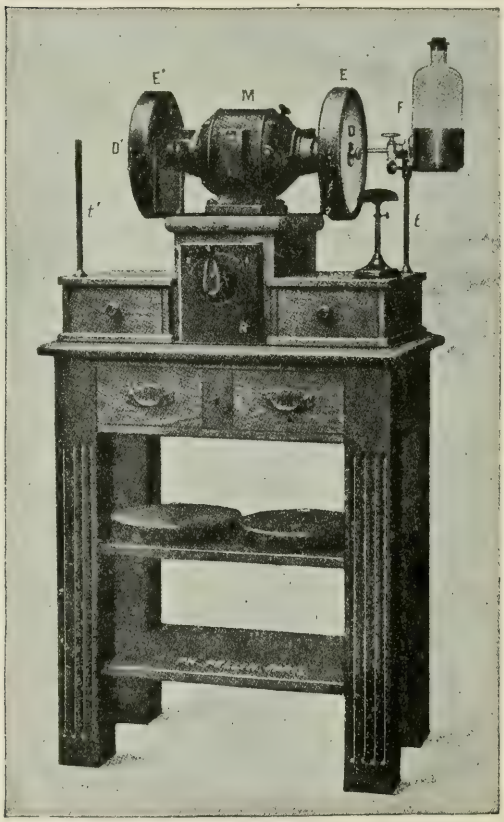


FIG. 7.—Hozizontal polishing machine.

D, D′, polishing wheels, protected by covers E, E′; F, alumina-water spray, supported on stands *t*, *t′*; M, motor; R, variable speed resistance.

The materials in common use as polishing powders are alumina, rouge (oxide of iron), washed emery, and chromic oxide.

Alumina, chromic oxide, and rouge may be obtained by calcining ammonia alum, ammonium bichromate, and iron oxalate respectively, or the pure oxides may be obtained from any chemical dealer.

In either case the material requires very thorough washing, followed by classification or grading. In France, alumina is in most general use. The most simple method of classification or grading is as follows: grind the specially calcined alumina into a thin paste with a little water, dilute with more water until the concentration is approximately 50 grms. alumina per litre and mix thoroughly. Allow to stand for 15 minutes before decanting the solution containing a certain proportion of alumina in suspension. The alumina in suspension may be used for polishing the harder metals and alloys (steels), or

the solution may be allowed to stand for two hours and again decanted. The alumina that then settles is suitable for polishing steels, and that still in suspension for the final polishing of brasses, bronzes, etc. If very soft metals are being examined, further decantations can be made and even finer products obtained. For general use, the two products mentioned will answer all requirements, the first (coarser) product for steels and the second (finer) product for the final polishing of brasses and soft metals after a preliminary polish with the coarser powder.[1]

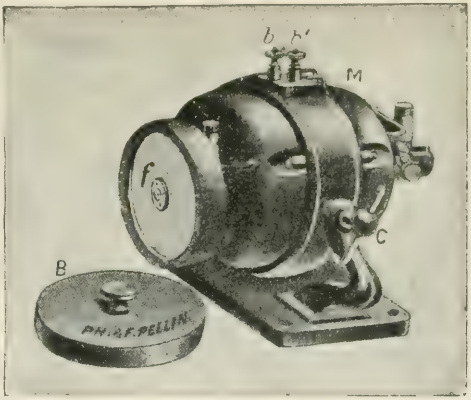


FIG. 8.—Polishing wheel mounted direct on motor.

f wheel; M, motor; *b*, *b'*, terminals; B, detachable cover.

Each grade of polishing powder will, of necessity, require a separate wheel, and too great attention cannot be given to cleanliness. Specimens before being transferred to finer wheels for further polishing must be thoroughly washed to remove the last traces of the previous powder.

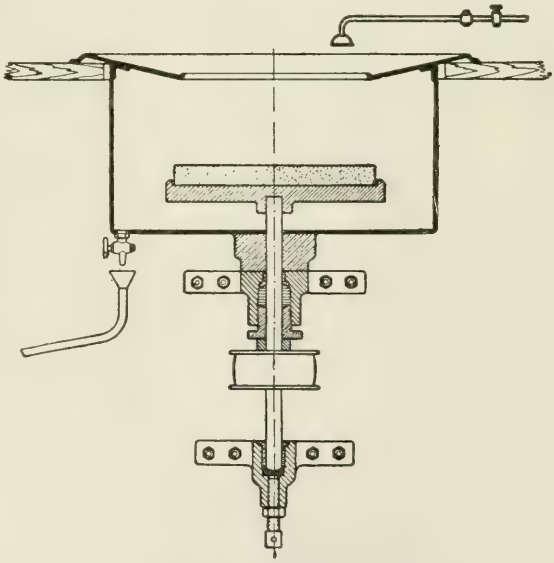


FIG. 9.—Horizontal polishing wheel, fitted with water spray and drain tap.

The number and nature of the abrasives depends mainly on the materials to be polished, the harder metals, although requiring more pressure, being naturally the easier to polish.

[1] Polishing forms a flow film on the surface of the metal—amorphous film (Beilby). In certain cases the formation of the film is avoided by means of what is known as polish attack, the etching taking place simultaneously with the polishing. Copper alloys may be successfully polished in this manner by the use of a mixture of chromic oxide and ammonia (Osmond and Cartaud).

Pl. II., Figs. 18–20, (p. 3) illustrate a specimen in the various stages of polishing and etching. The same portion of the specimen has been photographed in each case.

One of the authors, to illustrate the ease and rapidity with which a specimen may be prepared, gives a complete demonstration to his students during their course of instruction. Assuming a sample is chosen that can be easily sawn with a hand hack-saw, such as a bearing metal, the complete operation, including cutting off, grinding, polishing, etching, microscopical examination and photographic record, including development, occupies 12–15 minutes. Moreover, in certain works laboratories as many as thirty specimens may have to be examined per hour.

Many methods have been suggested to avoid the difficulties met with in attempting to polish very soft metals. Behrens has suggested the use of paraffin on the emery papers to act as a lubricant and prevent dragging ; Ewing and Rosenhain cast the lower melting point alloys on a sheet of polished plate glass and the higher melting point alloys (600°–1100°) on a polished steel plate. In order to avoid the frequent breakages that occur when using glass Hannover has suggested the use of a newly split mica sheet.

All these methods are open to criticism in the case of alloys, as they affect the rate of cooling and consequently the constitution.

It should be mentioned that alumina may be prepared by the amalgamation of aluminium : aluminium sheet or wire agitated with mercury and exposed to air is rapidly oxidised to alumina. The only drawback to this method of preparation is that the alumina produced is in an extremely fine state of division.

3. ETCHING

After polishing it is necessary to etch the specimen in order to reveal the structure.

It is impossible to give any general rules as to the choice of etching reagents. The ordinary chemical reactions are of assistance in selecting suitable reagents for the pure metals and less complex alloys. Thus, dilute potassium hydroxide gives excellent results with many alloys rich in aluminium ; but this is not always the case, and it should be recognised that many of the most commonly used reagents gave no indication of their utility before trial.

A brief description of the various methods of etching will now be given before proceeding with an account of the more important etching reagents and their uses.

Etching in Bas-relief.—This effect is frequently produced, a thick cloth on the polishing wheel being sufficient to cause its appearance. Under these conditions the softer constituents are ground

nitric acid in glacial acetic acid ($HNO_3 = d = 1{\cdot}32$); solution (*b*) equal parts of methyl, ethyl, and isoamyl alcohols. The two solutions are mixed immediately before use in the proportion: 1 part (*a*) to 3 parts (*b*). Only glacial acetic acid must be used.

This reagent gives a very slow and regular etching effect and has been used to distinguish troostite from the other constituents of steel.

(7) Acid ferric chloride solution. Grard has suggested the following compositions:—

(*a*) Brasses containing 67 per cent. Cu:

Water	100 c.c.
Hydrochloric acid, 22° Baumé ..	6 c.c.
Ferric chloride	19 grms.

(*b*) Brasses containing 90 per cent. Cu:

Water	100 c.c.
Hydrochloric acid, 22° Baumé ..	50 c.c.
Ferric chloride	5 grms.

Alcoholic solutions may also be used with advantage:

Alcohcl	750 c.c.
Hydrochloric acid, 22 Baumé	250 c.c.
Ferric chloride	34 grms.

The use of ferric chloride as an etchant for all alloys of copper, brasses, bronzes, etc., has become practically universal since its employment by Heycock and Neville in their joint research on the copper-tin series.

(8) Copper chloride solution: 10 grms. copper ammonium chloride in 120 c.c. water. Used for copper alloys and for developing the macrostructure of steels.

(9) Ammoniacal copper solution: This reagent gives better results, with copper alloys, than No. 8. It is prepared by adding ammonia to a solution of any copper salt until the precipitate at first formed is just redissolved.

(10) Dilute potassium hydroxide: This reagent is very useful for alloys rich in aluminium. The most suitable strength varies with different alloys, but as a general rule 50 per cent. potassium hydroxide solution, 36° Baumé, in distilled water is used. In some instances the addition of a few drops of hydrogen peroxide improves the results.

(11) Hot solution of sodium or ammonium hydroxide to which is added a few drops of hydrogen peroxide immediately before use. Used as a reagent for various copper alloys.

(12) Weak acids, chiefly dilute aqueous or alcoholic solutions of hydrochloric or nitric acids. (1 c.c. hydrochloric acid (dens. = 1·22)

to 200 c.c. water, suggested by Arnold: 1 c.c. hydrochloric acid (dens.=1·19) to 100 c.c. alcohol.)

(13) Dilute silver nitrate solution (2–5 per cent.): Useful for bearing metals; a black film is formed on the alloy which must be washed off with water.

The more common etching reagents are thus very few in number and may be easily prepared. The usual method of use is to immerse the specimen in the reagent contained in a small evaporating basin, petrie dish, or other suitable receptacle. In some cases it may be found more convenient to pour the reagent over the specimen placed polished face upwards in a dish; the dish may be rocked to and fro to ensure the even etching of the whole surface.

In either case the etching is stopped by washing in a jet of running water; if the specimen is porous or contains holes or cavities of any kind, this washing must be thorough to ensure the complete removal of the last traces of etching reagent and thus avoid any consequent staining. The specimen may then be dried in a current of air or by washing first in alcohol and then in ether. The polished face of the specimen must not be rubbed after etching.

4. MICROSCOPICAL EXAMINATION AND PHOTOGRAPHIC RECORD

A complete microscopical outfit for metallurgical work consists of three essential parts:

The illuminating apparatus;

The microscope;

The camera.

The examination of an opaque object has to be carried out by reflected light.

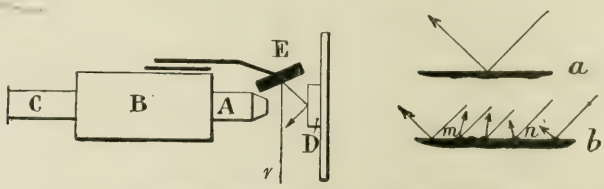


FIG. 10.—Oblique illumination by mirror (Goerens).
A, objective; B, microscope body; C, eyepiece; D, specimen; *r*, beam of light; E, mirror; *a*, polished surface; *b*, etched surface.

Brief descriptions of several metallurgical microscopes will now be given, but only the most general forms in use will be described; for further details and descriptions of other types of instrument the reader should refer to other works.[1]

[1] Sauveur, "The Metallography and Heat Treatment of Iron and Steel."

(*a*) Le Chatelier's microscope is, undoubtedly, the most used instrument of its type, and will be more fully dealt with than the other representative types.

(*b*) Nachet's apparatus.

(*c*) Marten's stand, used mostly in Germany and Switzerland.

(*d*) A portable metallographic outfit.

The method of illumination must first be considered. For visual observation the more usual illuminants are, the incandescent gas mantle, the carbon or metallic filament incandescent electric lamp, the half-watt lamp, the Nernst lamp, and, whenever possible, daylight (clouds).

For photographic work the mercury vapour lamp, of which a special pattern has been designed by Le Chatelier, or more often the arc lamp,[1] should be used. In fact, for metallurgical work, two independent sources of illumination are a great advantage; the one for visual observation, preferably a Nernst lamp; the other for photographic work, preferably an arc lamp.[2]

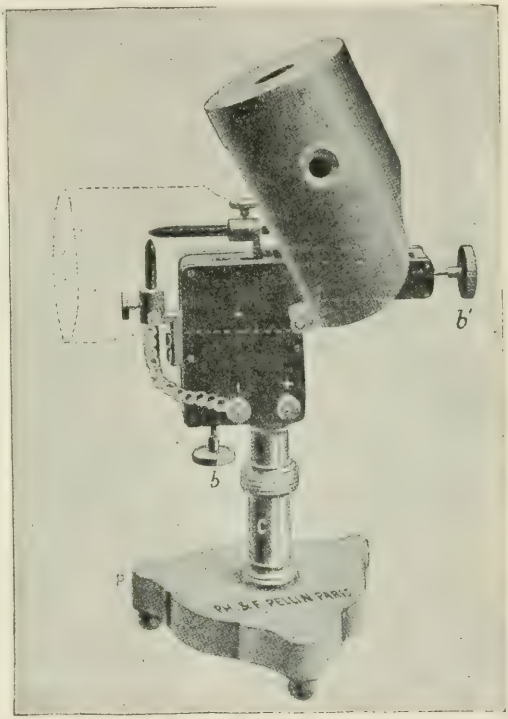


FIG. 11.—Arc lamp.

An ordinary form of arc lamp is illustrated in Fig. 11, the two carbons being hand fed. Automatic arc lamps are also used.

The light, from whatever source of illumination, is collected by a convex lens (condenser) which throws a parallel beam on to the illuminator, extraneous light having been obstructed by suitable diaphragms. If light of any given wave length is required, the beam is also passed through parallel-sided troughs containing suitable

[1] Translator's note: The 500 c.p. and 1,000 c.p. Pointolite lamps (Tungsten arc) are now largely superseding the arc lamp for this purpose.

[2] The arc lamp will serve equally well for visual observation, but the amount of light must be cut down by means of a light filter or ground glass placed in front of the condenser.

liquids as light filters, such as a saturated solution of potassium bichromate or picric acid (yellow filters).

The beam of light is finally thrown on to the specimen by means of a mirror (Fig. 10), a parallel-sided glass slip (Fig. 12), or a totally

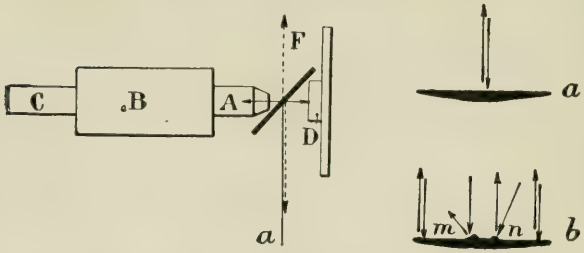


FIG. 12.—Illumination by parallel-sided slip.

A, objective; B, microscope body; C, eyepiece; D, specimen; *a*, beam of light; F, path of light rays passing through the slip; *a*, polished surface; *b*, etched surface.

reflecting prism (Fig. 13). The distinction between illumination by reflected and transmitted light is thus clearly shown by the different position of the mirror or other illuminating device.

With illumination by reflected light, the light is thrown on the face of the specimen, but with transmitted light it is thrown on the under side of the specimen. The illumination may be vertical or oblique, according to the relative position of the illuminator to the optic axis of the microscope.

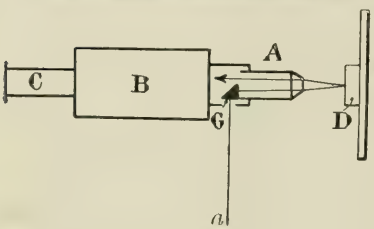


FIG. 13.—Illumination by totally reflecting prism.

A, objective; B, microscope body; C, eyepiece; D, specimen; *a*, beam of light; G, totally reflecting prism.

In the case of oblique illumination, which can be easily arranged by means of a mirror, a perfectly polished specimen would not reflect any light into the objective, as it would all be reflected obliquely in accordance with the laws of reflection, and therefore the surface would appear dark. But when the surface (*b*) has been etched in certain portions, some areas would be situated at such an angle that light would be reflected

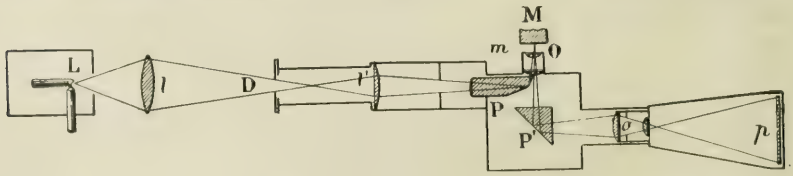


FIG. 14.—Path of the light rays in Le Chatelier's microscope.

into the objective, and these portions would appear bright in the dark ground mass of the unattacked metal.

(*a*) **Le Chatelier's Microscope.**—The chief features of the instrument are as follows :—

(1) The objective is inverted, the specimen being placed face downwards on the stage, which is situated above the objective.

(2) The horizontal body tube and eyepiece permit the observer to view the specimen whilst seated at the side of the instrument. The light is reflected into the eyepiece by means of a totally reflecting prism.

(3) The rotating prism allows the light to be reflected to the eyepiece for visual observation, or, by rotating the prism through 90°, down another tube, through a projection eyepiece, to a ground glass screen at the end of the camera.

In the earlier forms of the apparatus the camera was placed in a vertical position underneath the stage, allowing the light rays a

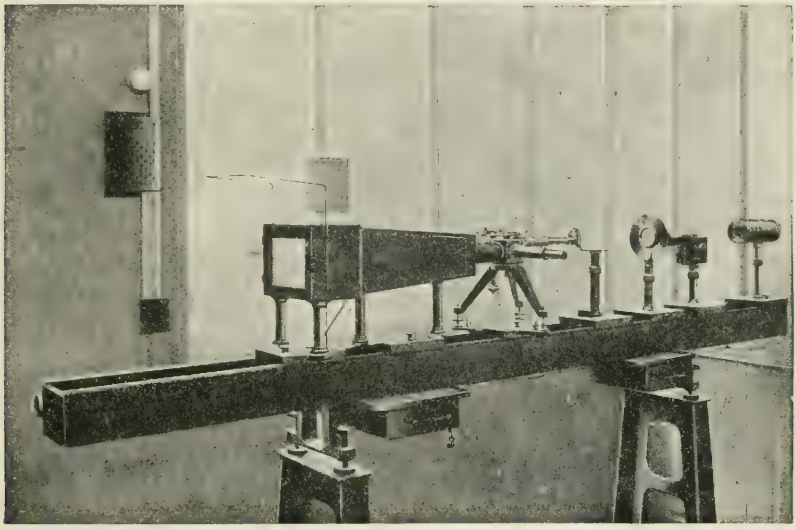


FIG. 15.—Le Chatelier's metallographic apparatus.
From left to right: Camera, microscope, condenser, arc lamp, Nernst lamp.

straight path from the objective through the projection eyepiece to the ground glass screen. This arrangement has since been modified to its present form, as focussing was found to present great difficulties in the original apparatus.

(4) Focussing by movement of the entire stage and specimen without disturbing the illumination, etc.

Fig. 14 illustrates diagrammatically the path of the rays through the apparatus.

The light from the arc lamp L is collected by the condenser l and thrown into the microscope through the diaphragm D. It then passes through a second condenser l' on to the convex surface of the totally reflecting prism P. In some patterns of the instrument, the diaphragm D, the condenser l', and the prism P are mounted in a

separate tube attached to the side of the microscope. The light, reflected upwards by the prism P, passes through the inverted objective O on to the specimen. Reflected by the specimen the rays again pass through the objective on to the second prism P′, by which they are reflected at right angles into the projection eyepiece *o* and pass to the ground glass screen *p*.

It should be observed that the rays are not absolutely vertical as they enter and leave the objective; this is essential if the two prisms P and P′ are to work satisfactorily. The prism P′ can be rotated through 90° to allow the rays to be reflected down the body-tube to the eyepiece for visual observation.

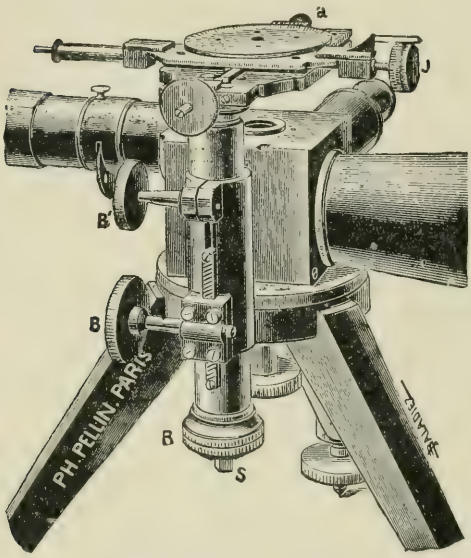


FIG. 16.—The stage, Le Chatelier's microscope.

a, J, C, milled heads operating rotating and traversing movements of the stage; B, milled head operating rack and pinion focussing; S, fine adjustment; B′, clamping crew.

Focussing.—The specimen, which is polished on one side only, is placed face downwards on the stage above the objective. The stage, in the more modern forms of the apparatus, is supported on three columns (Fig. 17). The earlier forms had a tendency to bend and could not be used for heavy specimens (Fig. 16). Focussing is carried out by raising or lowering the stage by means of a rack and pinion for coarse adjustment, a micrometer screw for fine adjustment. The specimen is roughly focussed with the coarse adjustment, which is then clamped and the fine adjustment used for obtaining the exact focus.

The adjustment is made by turning the milled heads when viewing the specimen through the visual observation tube or by means of a flexible extension when focussing on the ground glass screen for photographic work.

In order that different portions of the specimen may be examined the stage is made to rotate and traverse in two directions at right angles; all three movements being made by micrometer screws operated by milled heads. Graduated scales are provided on both movements, each division of the scale corresponding approximately to $\frac{1}{200}$ mm. movement of the specimen. Thus, by this means, the specimen may be easily removed and replaced in exactly the same

position, assuming its position on the stage is fixed. The fixed position on the stage is arranged for by having two file marks on the side of the specimen which correspond with two adjustable knife-edged pointers fixed to the stage. This device is frequently of great utility in investigating fractures, etc., and in examining the effects of various reagents on the same portion of a specimen. A typical

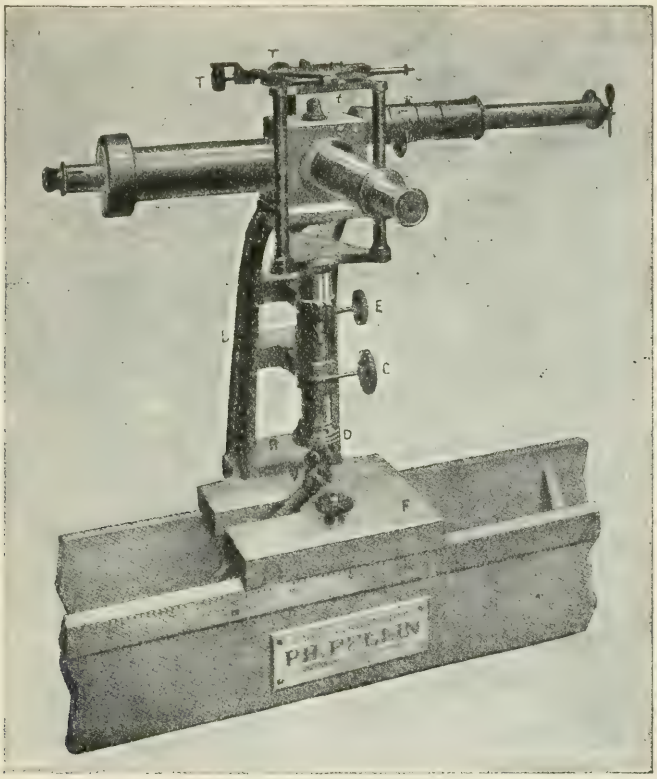


FIG. 17.—Le Chatelier's microscope. Latest pattern: stage supported on three columns.

F, stage; V, flexible extension for focussing on ground glass screen; B, microscope stand; C, milled head for rack and pinion; D, fine adjustment; E, clamping screw, T, T, *t*, rotating and traversing movements to stage.

example is given (Pl. II., Figs. 18–20, p. 3) in the case of a steel specimen containing two slag patches. The same pieces of slag can be seen in each case—after partial polishing and when polished—in the middle of the white area after etching.

The chief advantages of Le Chatelier's apparatus are: the ease of manipulation, the automatic levelling of the specimen which may be of any shape, and the possibility of examining large surfaces.

Nachet's Apparatus.—Apparatus of this type has been used by Guillemin, Osmond, and Charpy, all of whom have aided in its design and improvement. The apparatus may be best described as being

an ordinary microscope adapted for metallurgical work by the addition of special illuminators. The objective and eyepiece are placed at the opposite ends of the body of the microscope in the same axis, the stage being situated below the objective. Focussing is obtained by moving the tube relatively to the stage, preferably by moving the stage and leaving the microscope tube and camera stationary. The specimen is mounted in "plasticine" on a glass slip, levelled, and fixed on the stage with the usual clips (Fig. 23). It is essential that the specimen shall be perpendicular to the optic axis of the microscope, and the art of making this adjustment by hand can only be acquired by experience, but the operation may be simplified by the use of parallel-sided brass rings fitting against a shoulder on the objective; the specimen mounted in soft plasticine, on a slip, is pressed up against the objective after having been clamped on the stage.[1] Two methods of illumination are employed. One form of illuminator consists of a parallel-sided slip of glass (G) fitted into the body as shown in Fig. 21 (Cornu's arrangement). Charpy added a right-angled prism (P) to this illuminator, this addition permitting the body tube to be moved longitudinally without disturbing the illumination. This illuminator, much used in the past, is now obsolete.

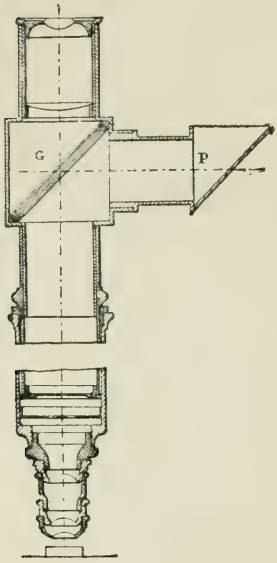


FIG. 21.

The second and more recent form, known as Nachet's illuminator, consists of a right-angled prism placed immediately above the objective (Fig. 22). The illuminant, condensers, etc., are placed at right angles to the microscope. The prism, which covers a portion of the back lens of the objective, reflects the light through the objective to the specimen. The illumination being nearly vertical, the light is reflected back through the objective to the eyepiece. The specimen is focussed by movement of the stage; the body tube, illuminator, etc., remaining stationary.

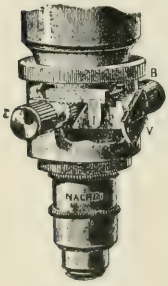


FIG. 22.

The older patterns of this instrument had the camera fitted in a vertical position supported on two columns, a light tight telescopic connection being made with the microscope above the eyepiece. The camera was lifted and turned on one

[1] Translator's note: The specimen may be easily and accurately levelled by the use of an instrument designed by Dr. Rosenhain (*Inst. of Metals*, vol. xiii. 1915).

of the vertical supports when visual observations were to be made (Fig. 23).

This form of apparatus suffers from the great disadvantage that

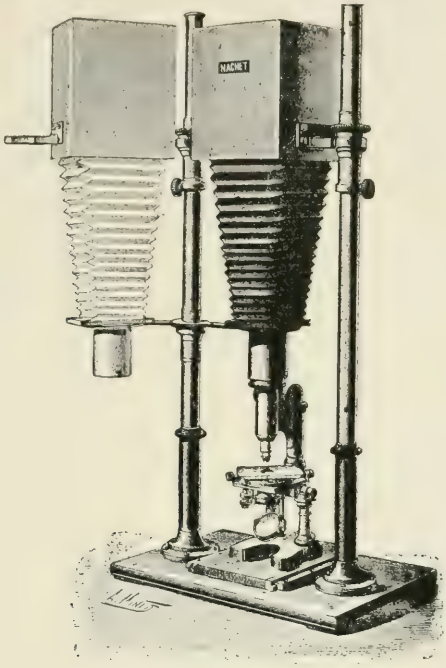


FIG. 23.

long camera extensions cannot be employed without great inconvenience to the operator, owing to the difficulty of focussing on the ground glass screen.

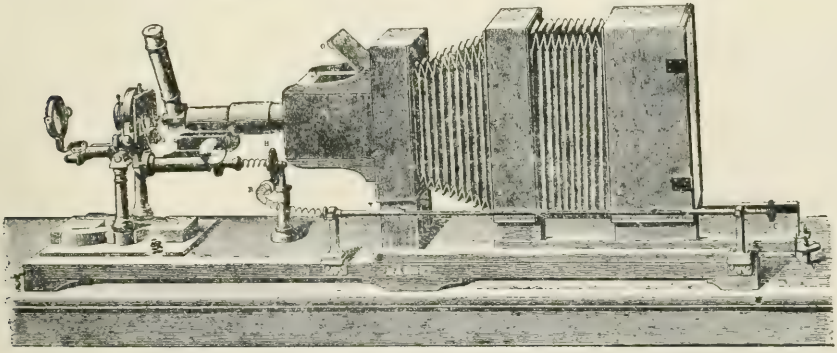


FIG. 24.

Messrs. Nachet have now overcome this difficulty by placing the microscope and camera in a horizontal position, and visual observation is obtained by interposing a second body-tube, fitted with a totally reflecting prism, immediately behind the prism illuminator (Fig. 24).

Martens' Stand.—This instrument is not used in France.

The principle of the instrument is as follows: The microscope can only be used in the horizontal position, and is designed to have exceptional rigidity in this position. The objective A and the eyepiece B are mounted in the body-tube E. The specimen N is mounted on the glass slip O, held in position by the clips PP. The stage Q can be levelled by the screws, *a*, *a*, so that the surface of the specimen N is perpendicular to the optical axis of the microscope. Focussing is carried out by moving the whole stage W′ in the slide *g* by means of the milled head Y. Fine adjustment is obtained by means of the rod *f*, working through the reduction gearing *e* to the wheel Z. A further adjustment, to allow of larger variations of

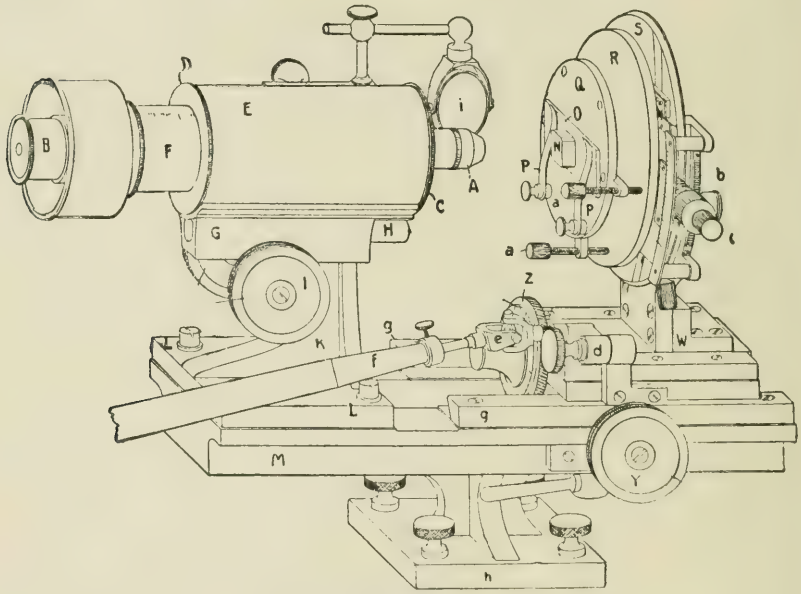


FIG. 25.—Martens' stand.

working distance between the objective and specimen, is provided by the rack and pinion GH, operated by the milled head I. The inner sliding tube F allows objectives of different tube lengths to be easily interchangeable. Illumination for low power objectives (photographic objectives) is effected by means of a mirror or parallel-sided slip, for oblique and vertical illumination respectively, mounted in the position *i*. For higher magnifications a Nachet pattern prism illuminator is employed, mounted immediately behind the objective as described in Nachet's apparatus.

Complete Portable Metallographic Outfit.—This outfit has been designed to enable metallographic investigations to be made when away from the laboratory; it contains all the necessary apparatus for polishing, etching, and visual observation, but no photographic

attachment is included. The outfit is contained in a box of convenient size. A small motor is provided to rotate a flexible shaft, on the extreme end of which the small grinding wheels and polishing discs are fitted by means of bayonet catches.

The wheels although small are amply large enough to enable specimens to be very quickly prepared. The set also includes dropping bottles, containing the more usual etching reagents, a small alumina-water spray, and several objectives and eyepieces of various magnifications. The microscope, which is of the vertical

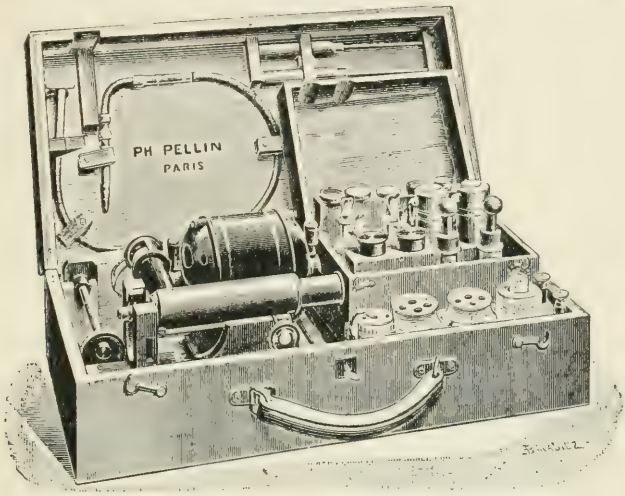


FIG. 26.—Complete portable metallographic outfit.

type, is so constructed that it can be fixed to any object that may have to be examined. Le Chatelier's illuminator is employed, a small lamp being permanently attached to the microscope.

Objectives used for Metallography.—The objectives in use are of three types: aplanatic, achromatic, apochromatic, which have a lower or higher degree of correction for chromatic and spherical aberration. The following table of magnifications gives the approximate magnification obtained on the photographic plate when using various objectives with Le Chatelier's outfit.

MAGNIFICATIONS OBTAINED WITH LE CHATELIER'S MICROSCOPE.

Zeiss objective.	Camera length.							
	0 cm.	10 cms.	20 cms.	30 cms.	40 cms.	50 cms.	60 cms.	70 cms.
aa	31	36·4	38·3	42·5	46	50	55	58
AA	44	51	58	63	68	75	80	85
C	210	260	300	340	375	420	460	500
E	580	680	780	900	1100	1212	1230	1350
$\frac{1}{12}''$ oil immersion	870	1020	1170	1350	1650	1818	1845	2025

N.B.—This table shows the magnifications obtained with the objectives *aa* and AA without the projection eyepiece.
The last three objectives given in the table are used with the projection eyepiece.

CHAPTER II

THE THEORY OF METALLOGRAPHY—THE CONSTITUTION OF ALLOYS

1. INTRODUCTION

A METAL or alloy, polished and prepared in the manner described in the previous chapter and examined under the microscope appears, in most cases, heterogeneous; inasmuch as it consists of two or more constituents which have been differentially attacked by the etching reagents and are rendered distinctive by variations in colour, shape, and brightness.

The reasons for these differences in appearance must be examined. The variations may be due to the different chemical compositions of the various constituents or, assuming the chemical composition to be the same, to variations in the physical properties. The microscope, alone, is unable to supply a solution to this problem as it is impossible to isolate the various constituents seen under the microscope in order to carry out the necessary chemical and physical tests.

It is, however, essential to know whether a homogeneous chemical substance is being examined or whether the material contains several elements and consists of various chemical combinations. Consideration of the law governing the existence of such chemical mixtures—Gibbs' Phase Rule—will enable this information to be obtained. Once the chemical constitution of an alloy corresponding to a state of equilibrium is known, such alloys, in a state of equilibrium, may be microscopically examined and their structures defined. The typical structures of such alloys in a state of equilibrium having been established, the variations in the fineness of the structure of similar alloys may be examined, and in a like manner, alloys of the same chemical composition but not in equilibrium may be identified.

2. CHEMICAL HETEROGENEITY

Gibbs' Phase Rule—Equilibrium Diagrams—Equilibrium of a Heterogeneous System—Degrees of Freedom

The chemical constitution of a mixture of several elements or chemical compounds depends on several known factors. These are the independent variables of the problem, and the actual chemical

composition may be defined for any known and definite value of these variables.

A chemical system may or may not be subject to internal chemical reactions and modifications. It is said to be in a state of equilibrium or chemical inactivity when these reactions are completed; but if the conditions governing the system are now altered (*i.e.* the independent variables are altered in value) these internal reactions recommence and continue until a new state of equilibrium is arrived at corresponding to the altered values of the independent variables.

An example will enable this to be more easily understood. If there is introduced into a known weight of water a sufficient quantity of some soluble salt, this salt is dissolved by the water with a consequent alteration in the system, solution continuing until a given quantity of the salt is dissolved in the water and the solution has become saturated. The system is then in chemical equilibrium; but if the temperature is changed the equilibrium will be destroyed and there will be a further quantity of salt dissolved or precipitated according to whether the solution is heated or cooled. Temperature is therefore one of the limiting factors in this case and may be termed an independent variable, since it may be fixed at any definite value and a corresponding state of equilibrium found.

Similarly, if calcium carbonate is heated in a closed vessel CO_2 is liberated, and there is a system consisting of $CaCO_3$, CaO, and CO_2. The decomposition of $CaCO_3$ ceases as soon as the pressure of CO_2 reaches a certain definite value, but if the temperature is changed there is a further reaction within the system $CaCO_3—CaO—CO_2$ until a new state of equilibrium is reached corresponding to some different pressure of CO_2; that is, temperature is one of the factors affecting equilibrium. Inversely, if the temperature is kept constant and the pressure of a system, already in equilibrium is varied, there is a reaction, but this reaction continues only until the original pressure has been restored, when the system is again in equilibrium and the reaction ceases. The conditions governing equilibrium therefore introduce an interdependence between the temperature and the pressure of such nature that both these factors exert an influence on the internal reactions of the system, but a definite temperature is sufficient to define the conditions of equilibrium; inversely, if the pressure is kept constant, there is only one temperature at which the system is in equilibrium, and thus the pressure also defines the conditions of equilibrium. Thus, although there are two factors able to affect the equilibrium of a system, the alteration of either of them is sufficient to change the conditions of equilibrium, and there is only one independent variable, either the temperature or the pressure, the choice of which is arbitrary. In the examples to be given in

this book the temperature will be considered as the independent variable in every case.

It is therefore essential to have a knowledge of all the factors that are capable of affecting the system; that is, the number of factors that are capable of varying independently of each other. These variable factors are known as the *Degrees of Freedom* of the system.

Phases.—The exact number of Degrees of Freedom that a system has under any definite conditions is stated by Gibbs' Phase Rule. The Phase Rule will only be considered in the present work as regards its application to the study of the constitution of metallic alloys; purely theoretical considerations will be omitted where possible, in order to avoid confusion. Before proceeding, however, the term *Phase* must be explained.

A system is said to be heterogeneous when it is composed of many homogeneous particles distinct from each other, which are therefore non-miscible, as miscibility would automatically tend to bring about homogeneity. Water and oil are not miscible and form a heterogeneous system, no matter whether the oil forms a separate layer on top of the water or whether the two are finely intermixed in the form of an emulsion; but in either case the two substances constituting the system may be described as two homogeneous chemical compounds: oil and water, which are not miscible, and the system is said to consist of two phases. In a similar manner a solid salt with its saturated solution consists of two phases—the solid salt and the saturated solution, and this solid salt may consist of a single crystal or a large number of entirely separate small crystals. Again, if the various elements or compounds of which the system is composed are able to form three, four, etc., homogeneous substances which are non-miscible with each other, then the system is said to consist of three, four, etc., phases. Thus, a phase is a homogeneous substance having a definite chemical composition and, in any heterogeneous system, two phases are distinct when, under the conditions governing the system, they are non-miscible, insoluble in each other, and, consequently, co-exist separately without chemical reaction until equilibrium is attained. They may in special circumstances have the same chemical composition.

The phases can be solid, liquid, or gaseous.

In the examples to be given the number of phases in any given system will be denoted by the letter P.

Application to Alloys—The Law of Chemical Equilibrium.—Let n represent the number of metals of which the alloy is composed,[1]

[1] Certain special cases (pseudo-binary alloys) in which the value of n, contained in the expression, is greater than the number of constituent metals have been purposely omitted.

P the number of phases in the system, and assume the pressure to be constant, this being generally the case in the study of alloys (this condition will be assumed in all further applications of the law), then the Degrees of Freedom (F), according to Gibbs' Phase Rule, are given by the equation

$$F = n + 1 - P$$

The law of equilibrium depending on the value of F, will therefore be a function of n and P; thus, in considering the phase rule as it applies to metallic alloys these will be the only two factors distinguishing the various cases to be considered.

According to the definition of Degrees of Freedom already given it follows that :—

1. If $F < 0$, equilibrium is impossible at any temperature;
2. If $F = 0$, equilibrium can only exist at one definite temperature;
3. If $F = 1$, any arbitrary temperature may be chosen and a corresponding state of equilibrium found for each case;
4. If $F = 2$, the temperature alone does not define the conditions for equilibrium to exist, another independent variable is required.

1. The Phase Rule applied to Pure Metals ($n = 1$)

(*a*) Only two phases can exist in equilibrium (F would otherwise be negative).

(*b*) Two phases can only exist at one definite temperature ($F = 0$).

This is the case of the solidification of a pure metal (the liquid and solid phases in equilibrium) which takes place at some definite temperature for every metal, this temperature being known as the melting point or freezing point of the metal. It is also the case when an allotropic modification occurs in a pure metal, such as an α modification being converted to a β modification insoluble in the former; then there is again a definite transformation temperature at which the two modifications α and β can co-exist in equilibrium.

2. The Phase Rule applied to Binary Alloys ($n = 2$)

(*a*) Only three phases can exist simultaneously in equilibrium (F must be $\geqq 0$).

(*b*) Three phases can only exist at one definite temperature ($F = 0$). Thus a system composed of the following phases: solid tin, solid bismuth, liquid bismuth-tin, can only be in equilibrium at one definite temperature (143° C.), and the composition of the liquid alloy may then be definitely determined, 55 per cent. Bi and 45 per cent. Sn.

(*c*) In the case of two phases in equilibrium ($F = 1$), the temperature is an independent variable. It may be chosen arbitrarily and

corresponding equilibrium conditions found for any definite temperature; but once the temperature is fixed the equilibrium conditions are completely defined and the compositions of the phases determined. Thus, during the solidification of a binary alloy, if the temperature is maintained at some definite value, the liquid and solid phases of the system slowly approach certain definite compositions corresponding to equilibrium conditions at that temperature. Further, when complete equilibrium is attained the relative proportions of the two phases are likewise defined. This may be illustrated in the case of an alloy of two metals A and B, containing X per cent. by weight of B: equilibrium being complete, the solid phase will have a definite composition and may contain, for example, X_s per cent. by weight of B; in a like manner the liquid phase will contain X_l per cent. by weight of B.

Suppose P to be the total weight of the alloy, P_s and P_l to be the weights of the liquid and solid phases, then

$$P = P_s + P_l$$

and

$$PX = P_sX_s + P_lX_l$$

therefore

$$\frac{P_s}{P_l} = \frac{X_l - X}{X - X_s}$$

P_s and P_l can be found from this expression.

In a similar manner the phase rule may be applied to alloys containing more than two metals, the number of degrees of freedom increasing, assuming the number of phases to remain constant, with the number of metals in the system. The great assistance that the application of the phase rule is able to give in the classification and solution of the chemical constitution of metallic alloys has now been shown, and its further application may be considered in the case of binary alloys or alloys of two metals. It must not be forgotten that the phase rule as previously described is applicable only to systems in a state of equilibrium, and that the only physical change has been a change of temperature. In considering the changes taking place in any system with alteration of temperature it is essential, if the results are to be of value, that the changes in temperature shall be so slow *that the various conditions passed through may be regarded as a continuous series of equilibrium conditions.*

Change of Equilibrium.—If, when a system is in equilibrium, one of the factors governing this state of equilibrium is altered, the equilibrium is destroyed and a new state of equilibrium tends to establish itself corresponding to this new temperature. This fact has been enunciated by Van't Hoff as follows: "In a chemical system in equilibrium any rise of temperature produces a transformation with absorption of heat, that is, it would bring about a lowering of the temperature if the reaction were self-produced; the

inverse being the case when the temperature is lowered." This law may be enunciated as follows: On heating all reversible reactions are accompanied by an absorption of heat, *i.e.* the reaction is endothermic, and on cooling they are accompanied by a liberation of heat—exothermic reactions.

Example: Cooling Curve of a Pure Metal.—The chief application of the heating and cooling curves of alloys is in the determination of the melting points and transformation temperature when present. Thus if an alloy is allowed to cool slowly and with a uniform loss of heat any sudden liberation or absorption of heat will be indicated by a change in the rate of cooling or heating. It will therefore only be necessary to measure the temperature as a function of the time and to represent the results graphically by a cooling curve with the time as abscissæ and the temperature as ordinates. Any irregularity in the curve denotes a sudden liberation of heat, and the temperature at which this sudden evolution takes place can be noted.

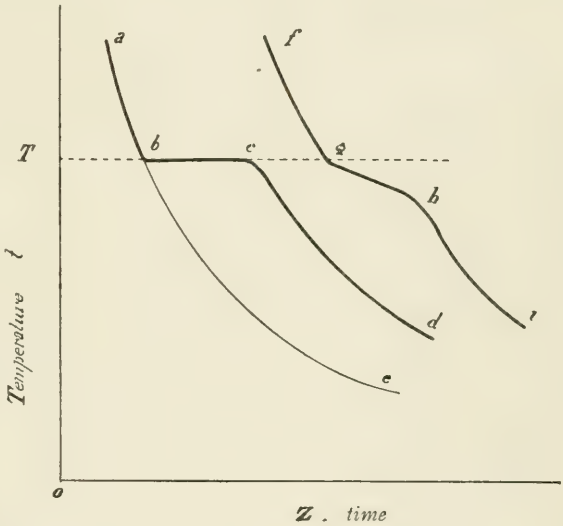


FIG. 27.

Take as an example a pure metal melted in a crucible and allowed to cool slowly in some suitable container maintained at a constant temperature, with a pyrometer inserted in the metal allowing the temperature to be observed continuously. In the absence of any internal evolution of heat the curve will have a perfectly regular form, as shown by *abe* (Fig. 27), for at any given instant, the rate of cooling is solely dependent on the temperature of the mass of metal and the external conditions (temperature of the container, cooling surface, thickness of crucible walls, etc.); but directly the metal commences to solidify, there is an internal liberation of heat. This liberation of heat accompanies the solidification of a portion of metal, so that the conditions of equilibrium may tend to be restored, that is, to re-establish the constant temperature for equilibrium conditions to exist between liquid and solid metal (melting point). This internal evolution of heat (known as latent heat of fusion) compensates for the external radiation losses

(assuming that the rate of cooling is not too great) in such manner that, as long as any liquid metal remains, the temperature remains constant and the cooling curve shows a horizontal line or *arrest bc*. Finally, on solidification being complete, the curve again commences to fall regularly along the line *cd*.

It has been shown that, from the point of view of the phase rule, an allotropic or polymorphic change in a pure metal gives identical results to the passage from the liquid to the solid state; thus, the transformation temperatures may be deduced from the cooling curves in a similar manner to the melting points. The cooling curve therefore offers a simple means of determining the melting points and transformation temperatures by observing the temperatures at which arrests such as *bc* occur. Further, the length of the arrest, other conditions being equal, will permit of an estimation of the total heat liberated.

The explanation given above as a reason for the temperature remaining constant during solidification requires that the heat lost by the body at any instant shall be exactly compensated by the heat generated, thus as the operation of cooling takes place more rapidly the conversion of liquid to solid metal must also be more rapid to compensate for the additional loss of heat at each instant; but the speed of solidification cannot increase indefinitely, so finally, with very rapid solidification, the conditions are such that the internal liberation of heat no longer compensates for the external losses and instead of an horizontal arrest *bc* (Fig. 27), there is only an alteration in the direction of the curve such as *gh*. The rate of cooling must therefore be sufficiently slow to enable a well-defined melting point to be observed.

This is more evident in the case of allotropic modifications. Chemical reactions taking place much more slowly in completely solid systems, it is rarely possible to obtain an horizontal arrest as with liquid solid systems, and in such instances the temperature *g* which marks the commencement of the change of direction *gh* in the curve is the temperature of transformation. It is in this manner that the transformation temperatures of iron must be determined. The experimental methods for the determination of cooling curves do not come within the scope of the present work and may be found fully dealt with in any treatise on Pyrometry or Thermal Analysis.

Only the main principles will be explained in the present instance in order that the methods used in the construction of equilibrium diagrams may be understood. It is now possible, with the information to be obtained from the phase rule, to examine successively the melting points and internal transformations taking place in alloys, and thereby to obtain the necessary information as to their chemical

constitution. The melting point is of primary importance, as alloys are nearly always prepared by melting their various constituents; therefore their condition is largely dependent, either directly or indirectly, on the conditions at the time of solidification.

SOLIDIFICATION OF BINARY ALLOYS

The Liquid State.—Given a mixture of several metals, a temperature can always be found at which the whole mass becomes molten. It must, however, be recognised that during any process of melting at atmospheric pressure there is the possibility of losses taking place owing to the partial volatilisation of some of the constituents. This loss increases with a rise of vapour tension of the alloy and, in practice, the composition of the alloy obtained generally differs from the theoretical figure given by the weights of the metals melted; the composition of any alloy must therefore always be checked by chemical analysis.

Consider an alloy of two metals A and B: its percentage chemical composition will be defined by the percentage amount of one of the two metals, B for example, contained in the alloy; let x equal this value, termed the *concentration* or chemical composition of the alloy.

NOTE.—All diagrams in this work will have the concentrations plotted as abscissæ and temperatures as ordinates.

When two molten metals are mixed together there are three possible conditions.

1. The two metals are completely miscible, completely soluble in each other, and form a single homogeneous liquid, a single phase similar to the case of water and alcohol.

This is the case of nearly all industrial alloys with but few exceptions (bronzes with high lead content).

2. The two metals are completely insoluble in each other, as in the case of aluminium and lead. In such instances after a certain length of time they will separate in layers as in the case of water and oil, the metals being superimposed according to their relative densities.

3. The intermediate case occurs when the two metals are partially miscible in the liquid state; two phases then exist in the liquid state, each of which contains the two metals A and B. It follows from the phase rule that at any given temperature the compositions of both phases are fixed when the system is in equilibrium, and the compositions of the two phases will then be defined by the concentrations x_1 and x_2, that is the percentage by weight of B which they contain.

This may be graphically represented in a similar manner to the

previous case by plotting the temperatures as ordinates and the corresponding concentrations as abscissæ (Fig. 28).

Thus at the temperature t, shown by the horizontal line BC, the two points B and C, abscissæ values x_1 and x_2, represent the two phases in equilibrium that can exist at that temperature.

It follows from the above that if two phases are to exist, the average composition of the alloy must lie between the values x_1 and x_2. Similarly, the composition may be shown, graphically, to lie between B and C; if it lies outside the segment BC there will be but one homogeneous liquid phase as in the first case considered when the two metals were completely miscible in each other.

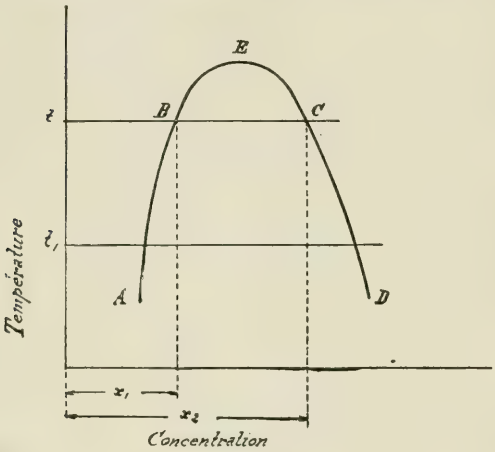


FIG. 28.

With alterations of temperature, the two points B and C are displaced along the two branches of the curve which unite at the point E; similarly to the previous case, the area enclosed by ABECD denotes the existence of two liquid phases and the area outside a simple homogeneous phase. If the temperature t falls to a temperature t_1, the compositions of the two liquid phases change, an exchange of the two metals A and B taking place between the phases constituting diffusion in the liquid state.

The alloys of zinc and lead offer a typical example of limited solubility, the property of only partial miscibility being utilised in the purification of these two metals.

This case being but rarely met with in industrial alloys it will be dealt with in as brief a manner as possible, and full consideration will be given to the first case of metals completely miscible with each other.

Solidification of an Alloy composed of Two Metals which are completely miscible in the Liquid State

The most general case is where the solid phase separating from the liquid contains both metals A and B, that is when A and B are miscible in the solid state.

(A) **Case of Metals completely miscible in the Solid State.**—Assume an alloy of the two metals A and B, containing x per cent. B, heated to a sufficient temperature to give a homogeneous liquid

and allowed to cool until complete solidification is effected. During the experiment the alloy is partly liquid and partly solid; it is, therefore, heterogeneous and at any given temperature the two phases, liquid and solid, will be able to exist in equilibrium as soon as the definite concentrations, denoted by x_s and x_l, for these phases have been reached.

This may be graphically represented by plotting the temperatures as ordinates with the concentrations as abscissæ (Fig. 29). An alloy of mean composition corresponding to the abscissa $OP=x$, will consist at a temperature t, under the conditions of equilibrium, of a liquid phase of composition $OP_l=x_l$, and a solid phase of composition $OP_s=x_s$. The corresponding points on the curve will be M_l and M_s. If the temperature is altered, the position of these points changes and there will be two curves (S) and (L) giving the compositions of the two phases in equilibrium for any temperature. If the temperature changes from t to t', for equilibrium to be re-established, there will be diffusion not only between the liquid and solid phases, but also within the respective phases.

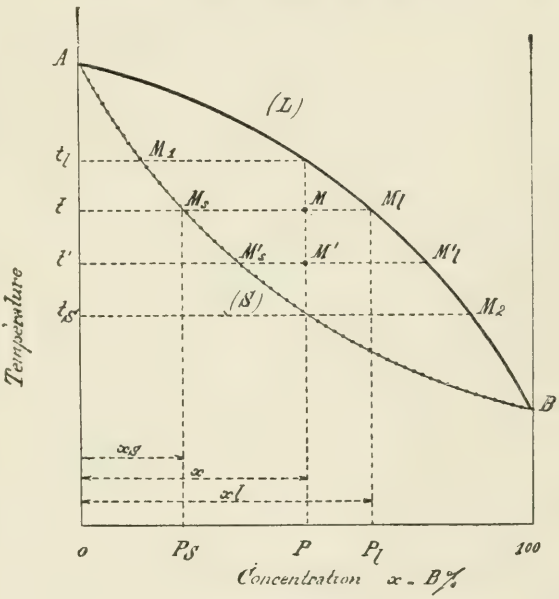


FIG. 29 (Type I).

Having regard to the fact that diffusion takes place much more readily in the liquid than in the solid state, it is evident that complete homogeneity is rarely attained in the solid phase; but as systems in a state of complete equilibrium only are considered in the present instance, this condition will be assumed and the effects of the slow rate of diffusion in the solid state will be dealt with at a later period.[1]

[1] Roberts Austen studied the rate of diffusion in the solid state in the case of gold and lead at different temperatures; even at atmospheric temperatures gold diffused in lead if the two metals were tightly clamped together; at 18° C. the rate of diffusion was 300,000 times slower than in the case of molten lead. Brani and Meneghini carried out diffusion experiments in the solid state in the case of copper and nickel. Spring, Cowper-Cowles, Masing, Desch, have also investigated similar effects. One of the authors with Victor Bernard published a paper on this subject in the Proceedings of the Société d'Encouragement pour l'Industrie nationale (*Bulletin* de mai, 1914).

As previously stated (p. 26) if x is the mean percentage composition of the alloy, the relation between the liquid and solid phases is given by the equation

$$\frac{p_s}{p_l} = \frac{x - x_l}{x_s - x} = \frac{\mathrm{MM}_l}{\mathrm{MM}_s}$$

This relation varies for every temperature, and it should be observed that the liquid phase ceases to exist at the temperature t_s where the curve (S) cuts the vertical line MP. This alloy will be entirely solid at that temperature, which is the temperature of complete solidification. Similarly the solid phase will be entirely absent at a temperature t_l, which is the point at which the continuation of the line PM cuts the curve (L), that is the temperature of complete fusion or the commencement of solidification.

The temperatures at which solidification commences are therefore given by the curve (L); this is called the "*liquidus*" or freezing-point curve; similarly, the curve (S) is called the "*solidus*" or melting-point curve, and gives the temperatures at which solidification is complete. This case differs from that of a pure metal, as solidification does not take place at any definite temperature but over a given range of temperature.

From the above laws it is possible to deduce the behaviour of any alloy of definite percentage composition x during the process of solidification; completely liquid above the liquidus (L), solidification commences as the temperature falls below the temperature t_l, the rate of solidification depending on the speed at which the temperature falls; at the same time, the compositions of the liquid and solid phases are continually changing in accordance with the curves (L) and (S) and, at any given instant, *assuming the system to be in equilibrium*, the composition and relative proportions of the phases present may be calculated. When the temperature t_s is reached, the liquid phase will have entirely disappeared and solidification will be complete. With further cooling, the composition of the solid phase is continually changing, due to internal diffusion between the various constituents of the solid phase in their attempt to maintain equilibrium conditions, and it is because of this property that the term *solid solution* has been applied to solid phases of this type; further, in the case of the liquid phase, owing to the rapid rate of diffusion, equilibrium is generally attained, but this is rarely so with the solid phase, having a much slower rate of diffusion and subject, as a rule, to comparatively rapid cooling. Therefore, at any given moment during solidification (assume a temperature t), there is a liquid phase of composition x_l, as shown by the curve (L), together with dendrites of the solid phase, the outside layers of which are of composition x_s but have the inner layers progressively

richer in the metal A. On the completion of solidification the solid phase has, in this case, a heterogeneous chemical composition consisting of layers of varying chemical composition radiating from the centres of solidification; the structure is therefore zonal or *dendritic*. This heterogeneity becomes greater as the rate of solidification, the speed of cooling, and the difficulty of diffusion are increased. But this condition is unstable (not in equilibrium), and the mass tends to become more homogeneous, as shown later in dealing with alloys not in a state of equilibrium (see p. 82).

It will be seen that the lines (L) and (S) divide the equilibrium diagram into three sections, the first above (L) in which the alloys are completely molten, the second between (L) and (S) where they are partially liquid and partially solid, and the third below (S) where they are completely solid. It will be observed that, if the mass is not homogeneous, the liquid phase will be richer in the metal B than is shown on the diagram, in which case the last drop of liquid to solidify will have a composition to the right of the point M_2, and consequently will solidify at a lower temperature because of its different composition. This subject will be dealt with later (see p. 82).

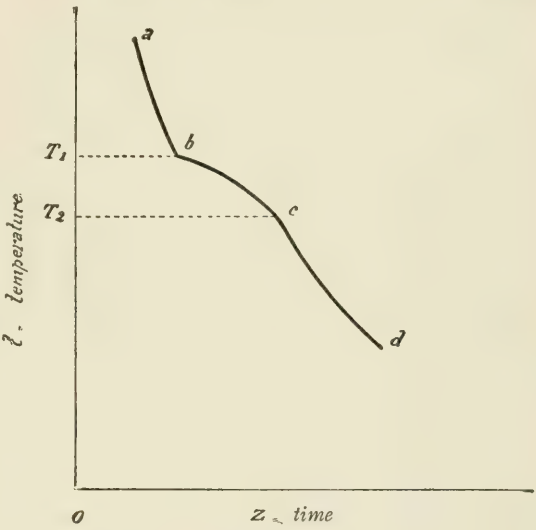


FIG. 30.

Cooling Curve of a Solid Solution (Fig. 30).—It has been shown that, at the melting-point of a pure metal, the cooling curve has an horizontal arrest (assuming the rate of cooling to be sufficiently slow). In the case of solid solutions there is always, in accordance with the general law relating to reversible reactions, a continuous evolution of heat between the temperatures T_1 and T_2, representing the commencement and completion of solidification, and consequently there is a change in the direction of the curve over the section *bc*, after which the curve again resumes its normal direction. The commencement and completion of solidification are indicated, theoretically at least, by the points *b* and *c*.

In practice these points are not clearly marked,[1] particularly in the case of the completion of solidification, and especially if the rate of cooling is not extremely slow.

Shape of the Liquidus and Solidus in the Case of a Solid Solution.

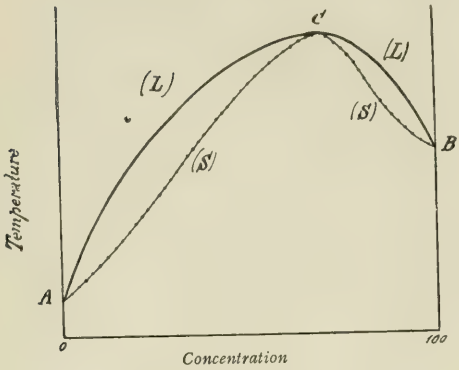


FIG. 31 (Type II.).

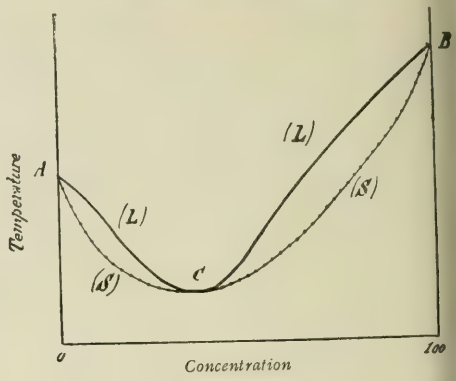


FIG. 32 (Type III.).

—Roozeboom has shown three representative types of equilibrium diagrams (Figs. 29, 31, and 32).

1. The solidus and liquidus meet at their extremities at points corresponding to the melting points of the pure metals.

2. Types II. and III. have a maximum or minimum point on the liquidus, the maximum or minimum value of the solidus being the same and at the same concentration,[2] the corresponding alloy behaves, during fusion or solidification, in a manner exactly similar to a pure metal, solidification taking place at a constant temperature; further, the curves have a common horizontal tangent.[3]

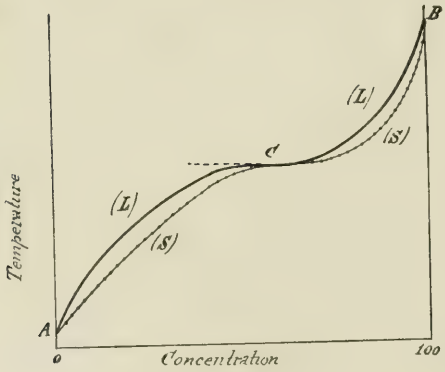


FIG. 33 (Type I*a*.).

It is possible for the solidus and liquidus to be so nearly the same that the difference between them is not measurable. Examples: alloys of iron and nickel, and copper-aluminium alloys containing

[1] In describing simplified theoretical examples, Rengade has shown *bc* to be the arc of an hyperbola, of which the concave side is towards the base of the diagram. The completion of solidification is therefore always less clearly marked than the commencement of solidification and may not be observable; the angle of intersection between the two branches *bc* and *cd* can be 180°.

[2] This will be more easily understood if it is remembered that the solidus should always be lower than the liquidus and that every position on the liquidus has a corresponding concentration on the solidus.

[3] Gibbs.

between 8 and 15 per cent. aluminium. To the three types already given must be added type I*a*, Fig. 33, described by Ruer,[1] having a horizontal tangent of inflexion. The following systems may be cited as examples of type I. (Fig. 29); iron-manganese, copper-nickel, silver-palladium, gold-palladium, gold-platinum, antimony-bismuth, copper-palladium, copper-platinum: as examples of type III.; gold-copper, gold-silver, manganese-cobalt, palladium-nickel, copper-manganese: and in type II.; the alloys of manganese and nickel and one of the solid solutions of the lead-thallium alloys.

B. **Case of Two Metals forming Two Solid Solutions (Partial Miscibility in the Solid State).**—The metals instead of being completely soluble in each other in the solid state or "*isomorphous*," as in the previous case, form two distinct solid solutions which are non-miscible. The

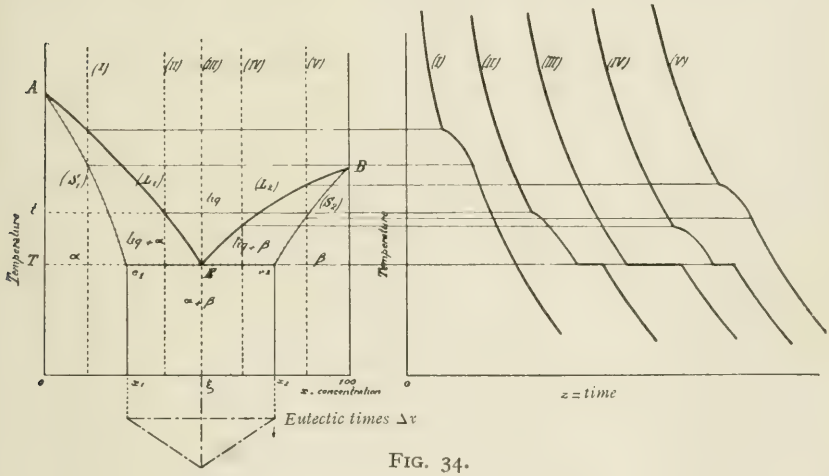


FIG. 34.

first, which may be called α, is formed in the alloys having a high content of the metal A; the second β, from those rich in the metal B (this condition is found more particularly when the two metals A and B are isodimorphous). In this case there exists a *limited range of solubility* in the solid state (Fig. 34).

The first solid solution α corresponds with a liquidus (L_1) and a solidus (S_1) commencing from the melting point of the pure metal A, and the second solid solution β with a liquidus (L_2) and a solidus (S_2) commencing at the melting point of the metal B.

The two liquidi (L_1) and (L_2) meet at a point E corresponding to a definite temperature T. It is therefore evident that at this temperature the liquid mixture, the composition of which is given by the abscissæ ξ from the point E is in equilibrium with a solid solution of composition x_1 given by the intersection of the horizontal, drawn through the point E with the solidus (S_1), and also in

[1] *Zeit. phys. Ch.*, LIX, I., 1907.

equilibrium with a solid solution of composition x_2 given by the point e_2 where the same horizontal intersects the solidus (S_2). The three phases of concentrations ξ, x_1, and x_2 are therefore in a state of equilibrium; but, as previously mentioned, in an alloy of two metals, the existence of three phases in equilibrium is only possible at one definite temperature T. Therefore, if the temperature rises above T or drops below T, one of the three phases will disappear. Two cases are possible, according to the respective positions of the branches of the liquidus, that is, according to whether the point E lies between the points e_1 and e_2 or is outside the segment e_1e_2. This may be alternatively defined according to whether the temperature T of the point of intersection E is lower than the melting points of the metals A and B, or lies between these two temperatures. Example: let x_1 be the concentration of the solid solution less rich in B, then $x_1 < x_2$; three conditions are possible:

$$x_1 < \xi < x_2 \quad \text{or} \quad x_1 < x_2 < \xi \quad \text{or} \quad \xi < x_1 < x_2$$

and there will be the respective equilibrium reactions:

$$\text{Liquid E} \rightleftarrows \text{solid } e_1 + \text{solid } e_2 \quad \text{or} \quad \text{solid } e_2 \rightleftarrows \text{solid } e_1 + \text{liquid E}$$
$$\text{or solid } e_1 \leftrightarrows \text{solid } e_2 + \text{liquid E}$$

since it is naturally only the phase of intermediate concentration which is able to split up and give rise to the other two phases.

The two types of diagram corresponding to these two cases are shown, and the points have received the names Eutectic point and Transition point. It must be observed that in the case of reactions taking place at a constant temperature T, if heat is withdrawn from a system in equilibrium and it is allowed to cool, owing to the principle already given (p. 26), a reaction will take place with evolution of heat tending to re-establish equilibrium at a temperature T. This will continue to occur until one of the phases has entirely disappeared; therefore, as the temperature T commences to change internal reactions occur to maintain it constant, these conditions continuing so long as three phases exist, the operation being analogous to that of the solidification of a pure metal and taking place under the same conditions.

1. **Eutectic Point.**—*The two branches* L_1 *and* L_2 *are above the horizontal drawn through the point* E [1] *and the point* E *lies between* e_1 *and* e_2 (Fig. 34).—In accordance with what has been already stated, at a definite temperature there will exist three phases—liquid E, solid e_1, and solid e_2—in equilibrium and, depending on whether there is a gain or loss of heat, the reversible reaction will take place as follows:—

$$\text{liquid E} \rightleftarrows \text{solid } e_1 + \text{solid } e_2$$

[1] T is lower than the melting points of A and B.

On cooling, the liquid E disappears at a *constant temperature* with the simultaneous formation of e_1 and e_2, and the solidification of the alloys takes place in the following manner :—

1. An alloy, the concentration of which lies outside the segment e_1e_2 ($> x_2$ or $< x_1$) ; the vertical line representing the alloy (vertical line I or V, Fig. 34) cuts the inclined branches of the liquidus (L_1 or L_2) and the solidus (S_1 or S_2) and solidification takes place as in the previous case (A, p. 30) with the formation of a single solid solution.

2. An alloy, the concentration of which lies between e_1 and E or between E and e_2 (vertical lines II or IV). The alloy represented by the vertical line II will be taken as an example, and the operation of cooling considered from the liquid state onwards. Solidification commences at a temperature t where the vertical line cuts the liquidus (L_1), continuing as in the previous case until a temperature T is reached, and at this temperature the solid solution, already formed, splits up into a solid solution of composition x_1 (point e_2) in a liquid of concentration ξ (point E). The loss of heat continuing, decomposition of the liquid E takes place, according to the reaction indicated above, with a simultaneous separation of e_1 and e_2 forming a mixture of which the individual particles are in a very much finer state of division than those of e_1 already existing at a temperature T. This finely divided mixture, which frequently appears under the microscope in the form of alternate lamellæ of the two phases e_1 and e_2 (see p. 74), is known as a *eutectic*, the line e_1Ee_2 is called the *eutectic horizontal*, and the temperature T the *eutectic temperature*.

The solidification of an alloy of composition between ξ and x_2, represented by the vertical line IV, is analogous to the above ; on passing the eutectic line there will exist crystals of the solid solution e_2 and of the eutectic e_1+e_2.

3. An alloy of concentration d_1 (vertical III). The alloy remains liquid until the temperature T is reached, the liquid E is then completely transformed at this temperature into a eutectic of e_1+e_2. Solidification takes place, in this case, at a constant temperature as with a pure metal or maximum of a liquidus, but, after solidification, there exists not a single phase but an intimate mixture of the two solid phases e_1 and e_2 ; the mean composition of this mixture being given by the abscissæ at the point E.

The above explanation applies entirely to cooling curves of the type illustrated by Fig. 34. In the case of all alloys forming eutectics there will be an arrest at the temperature T and, with identical conditions of cooling, the length of this arrest will be proportional to the quantity of eutectic formed at T°.

The eutectic horizontal e_1Ee_2 marks the completion of solidification

of all alloys, the compositions of which lie between x_1 and x_2. Below this line they consist of :—

$$\text{Solid solution } e_1 + \text{eutectic } (e_1 + e_2)$$

for the alloys between e_1 and E (intermediate concentration between x_1 and ξ) and of :—

$$\text{Solid solution } e_2 + \text{eutectic } (e_1 + e_2)$$

for the alloys between E and e_2 (intermediate concentrations between ξ and x_2).

Also, these alloys consist of only two phases e_1 and e_2 of concentration x_1 and x_2 distributed in a different manner according to whether the crystals of which they are composed were formed before or after the solidification of the eutectic.

It will be shown later that the concentrations x_1 and x_2 of the two phases e_1 and e_2 may vary after solidification is complete. It is because of this that the two lines joining e_1 and e_2 to the base of the Figure 34 have been drawn.

The solidus is the line $(S_1)e_1e_2(S_2)$; below the inclined sections (S_1) and (S_2) there is a single α or β solid solution, and between e_1 and e_2, a mixture of the α and β solid solutions, which, at the temperature T, have respectively the compositions indicated by the points e_1 and e_2. Further, x_1 and x_2 are the concentrations of the saturated solid solutions at the eutectic temperature.

II. **Transition Point.**—*The two branches of the liquidus L_1 and L_2 are on both sides of the horizontal Ee_1e_2 and of the point of intersection E and the point E is outside the segment e_1e_2* (Fig. 35).—Suppose the branch of the liquidus (L_1), giving rise to the first solid solution α, to be above the horizontal Ee_2e_1 and the branch (L_2) giving rise to the second solid solution β to be below Ee_2e_1, the corresponding solidi cut e_1e_2 at the points e_1 and e_2 which points give the compositions of the solid solutions α and β corresponding to a temperature T. At this temperature equilibrium exists between the three phases : liquid E, solid e_1, and solid e_2, and according to whether there is a gain or loss of heat by the system, the reversible reaction takes place as follows :—

$$\text{solid } e_2 \rightleftarrows \text{solid } e_1 + \text{liquid E}$$

assuming that $x_2 > x_1$.[1]

On cooling the phase e_2 is formed at the expense of e_1 and E ; this reaction is not completed, as when the latter reaches a concentration corresponding to e_2, that is, x_2, then :

[1] The inverse case $x_1 > x_2$ is very rare, but is met with in the copper-tin series. In this case, the alloy completely solid below S_1, again becomes partially liquid in passing through the transformation temperature, becoming entirely solid again below (S_2).

1. Between e_1 and e_2 the liquid E disappears and solidification is complete. The line e_1e_2 forms part of the solidus and, below T, the alloys consist of a mixture of the two solid solutions α and β having at a temperature T° the concentrations x_1 and x_2 at the points e_1 and e_2.

2. Between e_2 and E, e_1 disappears at the expense of e_2 and E, and solidification is not complete. Below the temperature T, the alloys consist of liquid and β solid solution having respectively, at a temperature T°, the concentrations x_2 and ξ at the points e_2 and E; solidification then continues as in the case of a single β solid solution by the progressive disappearance of the liquid.

The temperature T marks a rapid change in the composition of the solid phase in equilibrium with the liquid, the composition of

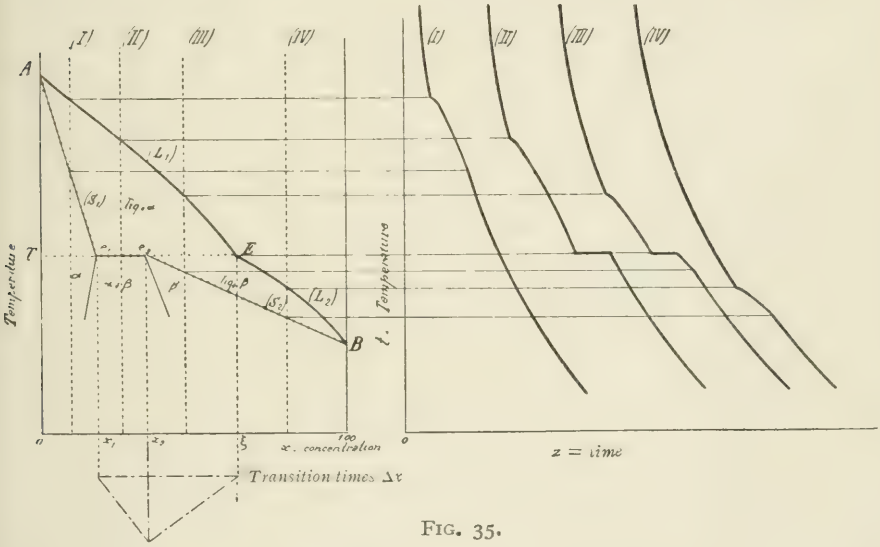


FIG. 35.

which changes from x_1 to x_2; above the temperature T it is the α solid solution which is stable in the presence of the liquid, and below it is the β solid solution. For this reason this temperature is termed the *transition point.* The solidus is therefore $(S_1)e_1e_2(S_2)$. Below this solidus the diagram is completed by two lines drawn from e_1 and e_2; lines denoting the mutual equilibrium of the non-miscible α and β solid solutions in the solid state, termed transformation lines. As in previous cases, the horizontal line e_1e_2E corresponds to arrests on the cooling curves at the temperature T and under similar conditions of cooling, the length of this arrest shows a maximum at the point e_2. Further, the portions of the cooling curves having the least inclination correspond to the region between the liquidus $(L_1)(L_2)$ and the solidus $(S_1)e_1e_2(S_2)$. Fig. 35 illustrates the four typical theoretical examples of these cooling curves

corresponding to alloys the percentage compositions of which are given by the vertical lines I, II, III, and IV.

Summary and Consideration of Special Cases.—It has been shown that the branches of the liquidus (L_1) and (L_2) corresponding to the formation of the two distinct solid solutions, α and β, may occur as one of the four types previously described (*see* Figs. 29, 31, 32, 33). The two previous cases may be considered either as two metals A and B partially soluble in each other or, alternatively, as two metals having an area of insolubility extending between the points e_1 and e_2.

This partial solubility may only be very slight, in which case the points e_1 and e_2 very nearly correspond to the compositions of pure metals.

In the case of the eutectic more particularly, the mutual solubility

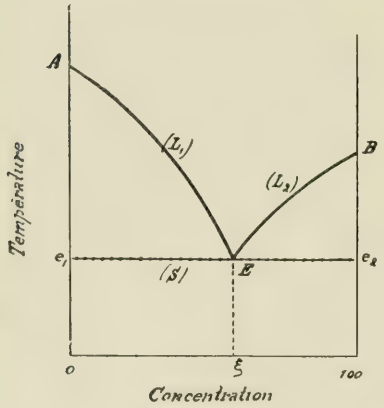


FIG. 36.

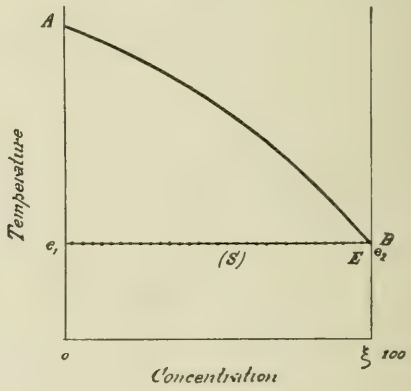


FIG. 37.

of A and B in the solid state may be practically nil. The diagram is then as shown in Fig. 36, the branch (L_1) corresponds to the separation of the metal A from the liquid and the branch (L_2) to the separation of the metal B; excepting the two pure metals, solidification is completed, in the case of all the alloys of A and B, at a temperature T on the horizontal e_1Ee_2 by the formation of a eutectic (A+B) of which the mean composition is given by the abscissæ ξ at the point E. In this instance, the metals A and B are *completely non-miscible in the solid state*, and all the alloys in the solid state consist of the eutectic (A+B) and A or B, according to whether the content of B is less or greater than ξ. There are only two phases, A and B.

This is the case with the alloys of silver-lead, bismuth-cadmium, bismuth-tin, cadmium-zinc, tin-zinc, etc. In certain instances (Fig. 37) the point E very nearly coincides with one of the constituent metals, in which case one branch of the liquidus appears to form the

eutectic point where it meets the boundary of the diagram (parimetal), and the eutectic temperature is then easily confused with the melting point of the pure metal. One of the authors [1] found this to occur with the copper-bismuth alloys.

C. **Metals forming Three Series of Solid Solutions as they pass from the Liquid State—Formation of a Compound.**—In this case there exist three branches of the liquidus (L_1), (L_2), and (L_3) corresponding to three solid solutions α, β, and γ; there are consequently three branches of the solidus (S_1), (S_2), and (S_3).

The form of the diagram will depend on:

1. The respective forms of the three branches (L_1), (L_2), and (L_3) of the liquidus corresponding to one of the four types previously described.

2. The arrangement of the branches round their points of mutual intersection will be in accordance with what has been previously described in the cases of the eutectic and transition points. Three typical examples of the various possible arrangements will be taken in illustration of this case.

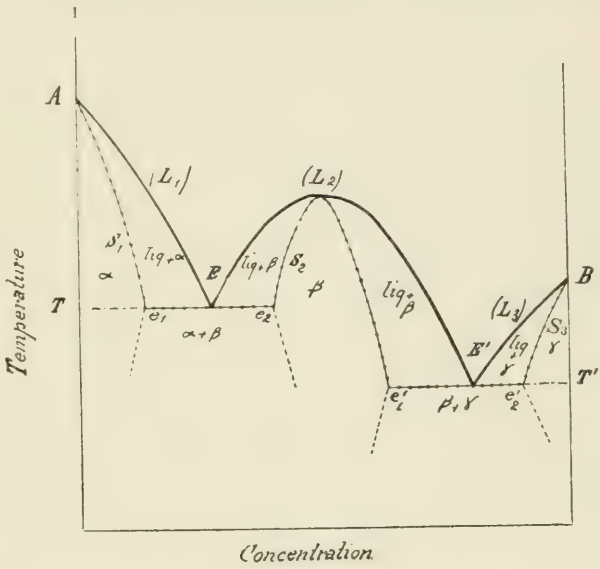


FIG. 38.

1. *There are two eutectic points E and E_1, the intermediate branch of the liquidus* (L_2) *being of the type II described by Roozeboom* (*Fig.* 38). —Two eutectics are formed, $\alpha+\beta$ and $\beta+\gamma$, at the temperatures T and T′ shown by the horizontals e_1Ee_2 and $e'_1E'e'_2$; the percentage compositions of these eutectics are given by the abscissa ξ and ξ' from the points E and E′ and of the constituents of these eutectics, α, β, and γ, by x_1 and x_2, abscissæ of e_1 and e_2 for the first eutectic $\alpha+\beta$ and x'_1 and x'_2 abscissæ of e'_1 and e'_2 for the second eutectic $\beta+\gamma$.

As in the previous case, it is possible for the miscibility in the solid state to be nil. This is particularly the case with the intermediate solid solution β which will then have a constant composition with

[1] Portévin, *Revue de Met.*, vol. iv., p. 1077; 1907.

variation of temperature, and the branch of the solidus (S_2) then consists of a vertical line $Me_2e'_1$ (Fig. 39) since this curve gives the composition of the solid in equilibrium with the liquid, in this case a constant. Therefore, a definite compound of the two metals A and B separates along (L_2) of composition $C=A^mB^n$.

The maximum point M corresponds to the melting point of the definite compound $C=A^mB^n$ having a content X of the metal B. When the alloy is of composition X the cooling curve will show a single arrest at the point M, the compound C behaving in a manner exactly similar to a pure metal.

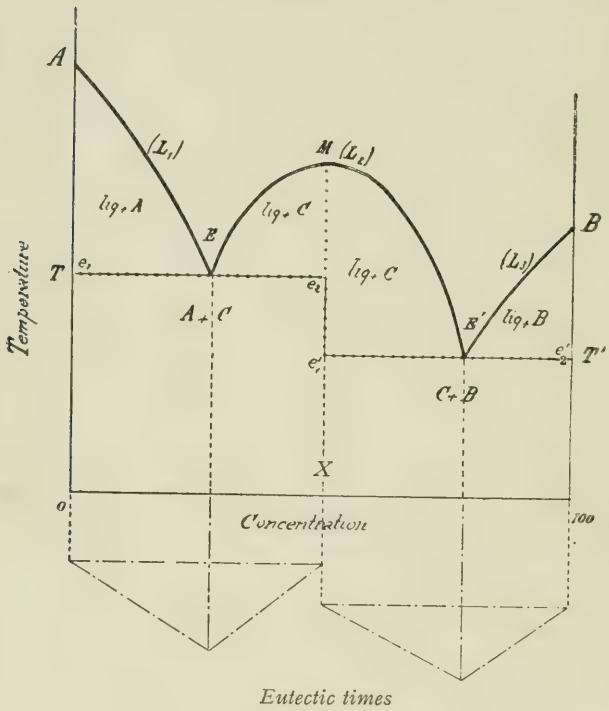


FIG. 39.

Along the branches of the liquidus (L_1) and (L_3) there separates either the solid solutions α and β, as in Fig. 38, or the pure metals A and B as in Fig. 39; in the latter case the solidus will simply consist of the two eutectic horizontals e_1Ee_2 and $e'_1E'e'_2$, and the alloys after solidification have the following constitutions :—

A+eutectic (A+C)

in the case of the alloys of lower concentration than ξ abscissæ of E ;

C+eutectic (A+C)

in the case of alloys of intermediate concentration between ξ and X ;

C+eutectic (C+B)

in the case of alloys of intermediate concentration between X and ξ, abscissæ of E' ;

B+eutectic (C+B)

in the case of alloys of greater concentration than ξ.

Finally, the two solid phases A and C exist in the alloys of lower concentration than X and the two solid phases C and B in the alloys of greater concentration than X.

The diagram may be considered as two separate diagrams united together; the one corresponding to the alloys of the metal A and the compound C, the other corresponding to the system composed of the compound C and the metal B.

In this particular instance the compound C, which melts without decomposition, is characterised by a maximum M on the liquidus and the absence of the eutectic arrest at the temperatures T and T′. With all the other alloys of the system a eutectic is formed and consequently the cooling curves show arrests at the temperature T and T′ (except the pure metals).

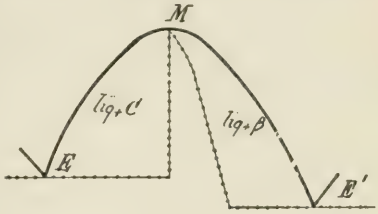


FIG. 40.

In some cases the compound also forms solid solutions, and the solidus is then of the type shown in the preceding figure. In other cases a solid solution is only formed on one side of the maximum (Fig. 40), and the compound C then separates along EM and the β solid solution along ME′.

2. *The case of a transition point E and a eutectic point E′* (*Fig.* 41).

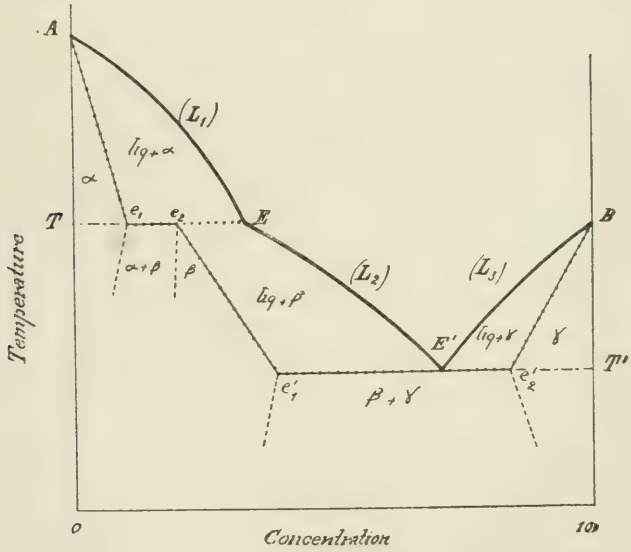


FIG. 41.

—Solidification, etc., will take place as previously described at the temperatures T and T′ of the points E and E′.

At a temperature T (horizontal e_1e_2E of the diagram), on further cooling β is formed at the expense of the solid solution α already existing (and which has reached the concentration x_1, shown in the diagram as the abscissæ of the point e_1) and of the liquid of

concentration ξ at the point E. This reaction absorbs either the remaining liquid E, or the already formed solid solution α, according to whether the composition of the alloy lies between e_1 and e_2 or between e_2 and E.

On further cooling at a temperature T′ (horizontal $e'_1E'e'_2$) the remaining liquid of concentration ξ, abscissæ of E solidifies completely with the formation of a eutectic of $\beta+\gamma$. As in the previous case, it is possible for the intermediate solid solution β to have a constant concentration with change of temperature, the corresponding branch of the solidus then being vertical (Fig. 42). This occurs when a compound

$$C=A^mB^n$$

of the two metals A and B, of composition X, separates along the liquidus (L_2). Consider now what takes place in this case and assume, to avoid complication, that there is no miscibility in the solid state and that the pure metals A and B separate along the liquidus (L_1) and (L_3).

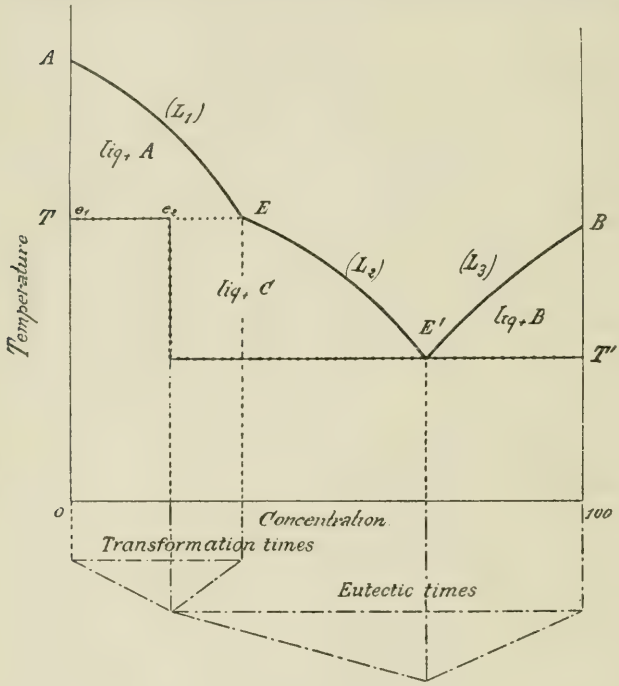


FIG. 42.

On cooling, at the temperature T of the point E, the compound C is formed by the reaction between the liquid E and the deposited metal A; inversely, on heating the compound C splits up into the metal A and the liquid E; *it decomposes before melting* and the compound has no melting point, thus differing from the previous case.

Finally, it is possible that along the branch EE′ is deposited, neither a solid solution nor a compound, but an allotropic form of the metal A; the vertical line at the point e_2 then closely corresponds with that at the point A.

General Remarks.—The equilibrium diagram obtained from the cooling curves, shows the formula of the compound. In order to establish the exact position of the corresponding vertical, Tammann has stated that under identical cooling conditions:

1. Compounds which are formed at transition points correspond with the alloy which, at the transition temperature, shows the longest arrest on the cooling curve.

2. When a compound forms one of the two constituents of a eutectic, the eutectic arrest shown by the cooling curve entirely disappears in the case of the alloy corresponding to the pure compound.[1]

This is shown by the portions of the diagrams below the base line (Figs. 39–42), and what has been stated in respect to systems forming three series of solid solutions α, β, and γ will apply equally in the case of 4, 5, etc., solid solutions; some or all of these intermediate solid solutions may contain definite chemical compounds.

In the cases so far considered, the systems have been completely miscible in the liquid state. As previously mentioned, this is not always the case and examples of the second type will now be considered.

Systems consisting of Two Non-miscible Liquids in the Molten State (Fig. 43)

It has been shown, when considering alloys in the liquid state, that metals may be non-miscible in the liquid condition, similarly to oil and water, or only partially miscible, as in the case of water and phenol. Also, in conformity with the laws of equilibrium for binary alloys of two metals with two phases (*see* p. 30), the area of two liquids was divided from the single liquid area by the curve MFN,[2] defining for any temperature the concentrations of the two liquid phases M and N in a state of equilibrium, these being the limiting concentrations outside which the alloys form a single phase in the liquid state.

As in previous instances, within the region of the two liquids, the relation between the masses of the two liquid phases is given by the equation:

$$\frac{\text{Liquid N}}{\text{Liquid M}} = \frac{\text{PM}}{\text{PN}}$$

Outside the curve GMFNH, that is in the region of a single liquid phase, solidification takes place in the ordinary way; assume, in order to avoid complication, that the solidification takes place by the separation of the two pure metals and the final formation of a eutectic E.

[1] For further details as to this method of determination, see Portévin, "La Méthode d'analyse thermique du professeur Tammann" (*Revue de Met.*, vol. iv., p. 797; 1907).

[2] As a general rule, the two branches of the curve GM and HN approach one another with rise of temperature and unite at a point T corresponding to the critical temperature of the double liquid mixture.

Passing from the melting point of one of the pure metals A, a branch of the liquidus AH indicates the separation by primary solidification of the metal A ; but when the temperature T is reached, this branch AH meets the line HF which defines the region having two liquids ; at this temperature T, the liquid at concentration H is in equilibrium with :

1. The solid metal A since the point H is on the liquidus AH.

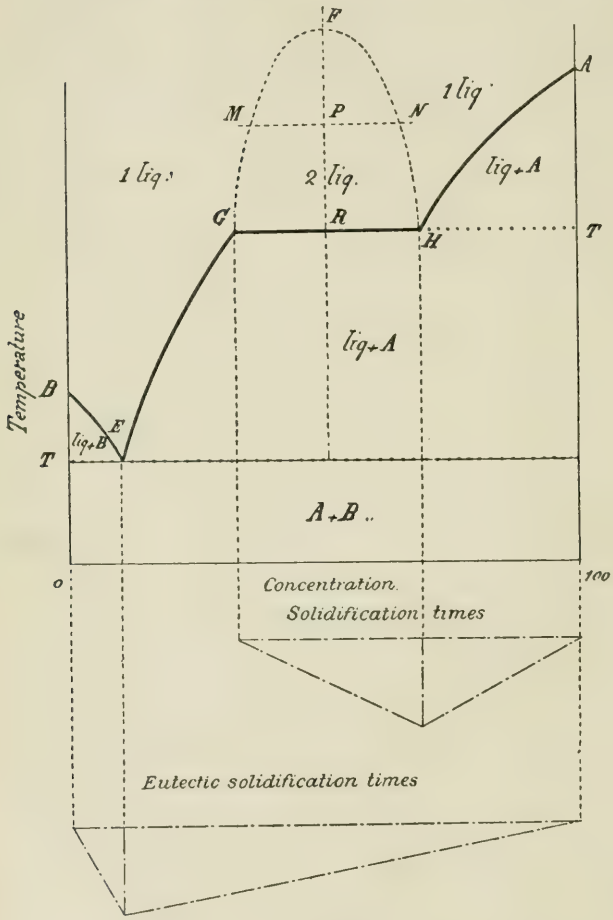


FIG. 43.

2. A second liquid phase of composition G, since the point H is also on the curve HFG.

The three phases : liquid H, liquid G, and solid A, are then in equilibrium ; in accordance with what has been previously stated, this state of equilibrium can only exist at one definite temperature T ; if heat is removed from this system of three phases, or, in other words, if the alloy is allowed to cool, there will be a reaction between the phases and a consequent liberation of heat tending to restore the temperature T. But H being the intermediate phase between G and A, only the following reaction can take place :

$$\text{Liquid H} \rightleftarrows \text{liquid G} + \text{solid A}$$

The two phases H and A having existed above the temperature T, the liquid H will split up depositing more solid A and forming more liquid G, and this reaction will continue at a constant temperature until the liquid H has entirely disappeared. There will then be left only a liquid phase G and a solid phase A, and solidification will

continue in the ordinary way along the branch GE of the liquidus. The liquidus includes an *horizontal section* GH indicating the region where solidification takes place with two liquids present, and the extremities G and H give the compositions of the two liquid phases at the temperature T.

An alloy of composition P, intermediate between G and H, consists, in the liquid state, of two phases M and N; allowed to cool, at a temperature T, the two phases approach the compositions G and H and are present in the proportion $\frac{RH}{RG}$; then the reaction given above occurs until the liquid H ceases to exist; during this reaction the temperature remains constant (if the cooling is not too rapid). All alloys having compositions between G and H show an arrest on their cooling curves, which indicates the latent heat of decomposition of the liquid H and is consequently a maximum when the entire alloy takes part in the reaction; this occurs at a mean concentration corresponding to the abscissæ at the point H.

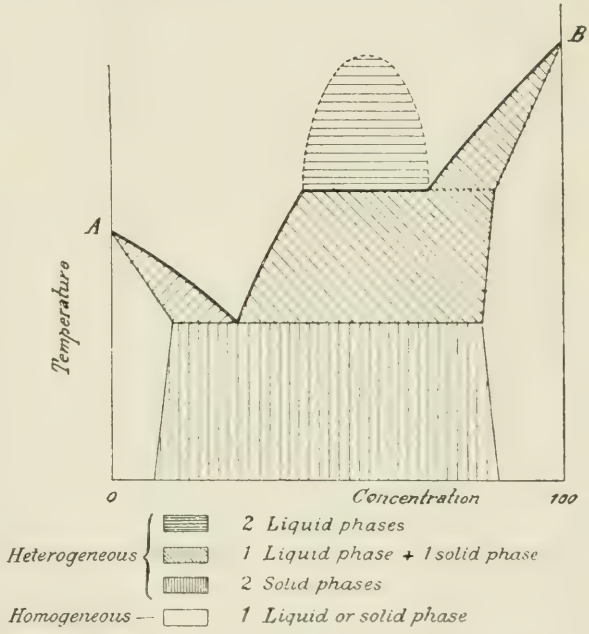


FIG. 44.

The following systems offer examples of this type: copper-lead, nickel-lead, silver-nickel, zinc-lead, zinc-bismuth, etc.; it is possible for the two metals to be entirely insoluble in the liquid state, in which case they solidify separately and the solidification or melting point curves are reduced to two horizontal lines passing through the melting points of the two metals. Examples: aluminium-lead, iron-lead, silver-iron, etc.

In Fig. 44, in which two metals A and B are shown partially miscible in the solid state, the areas in which two phases exist are shown sectioned; horizontal sectioning in the case of two liquid phases; vertical in the case of two solid phases, and oblique where there is one liquid and one solid phase.

TRANSFORMATIONS IN SOLID ALLOYS

Having considered the chief cases possible in the solidification of binary alloys, or in other words, the equilibrium conditions between the liquid and solid states (crystalline state as will be shown later), the phenomena occurring in completely solid alloys will now be briefly considered.

The internal chemical constitution is able to change, by various transformations occurring after solidification has taken place, in such manner that the properties and structure of the alloy are entirely altered.

In the examples, the transformations considered will have completed themselves in a normal manner, or stated in other words, equilibrium conditions will be assumed. In practice, various retarding influences, which may be classified as internal passive resistances, due to the viscosity of the medium, frequently prevent these conditions from being fulfilled. Also, after having defined the equilibrium conditions, the effect of the various retarding influences, which tend to retain the alloys not in equilibrium and lead to various theories on the quenching of alloys, will be considered.

The laws governing these transformations are identical with the laws governing solidification and are interpreted by analogous curves. The principal cases will be dealt with and compared with those found for the solidification of alloys.

1. **Polymorphic Transformations in a Pure Metal or Definite Chemical Compound.**[1]—It has been shown that solidification can occur without internal chemical change, viz.: solidification of a pure metal or of a definite chemical compound corresponding to a maximum of the liquidus; the two phases present then have the same chemical composition, for it is a simple change of the physical state. But the same definite chemical substance can exist, in the solid state, in two varieties entirely different as regards their crystalline form and also as regards their properties, giving rise to two phases in equilibrium at a certain definite temperature under exactly analogous conditions to the melting point; *this temperature is the polymorphic or allotropic transformation temperature under equilibrium conditions.*

The different varieties are frequently distinguished by the various Greek letters α, β, and γ; for example:

1. Iron exists as three varieties α, β, γ; the equilibrium or transformation temperatures of which are

$$\alpha \rightleftarrows \beta : 769^\circ$$
$$\beta \leftrightarrows \gamma : 917^\circ$$

[1] To this may be added, a solid solution corresponding to the maximum point on the solidification curves.

2. Tin exists as three varieties: amorphous grey tin stable at 20° C. (Cohen) with tetragonal tin which is in turn transformed at 170° into white rhombic tin (Werigin, Lewkojeff, and Tammann).

3. Zinc exists as two varieties, the transformation taking place at about 360° (Le Chatelier).

4. Thallium shows a polymorphic transformation at about 226° (Levin, Williams).

5. Nickel has a magnetic variety α and a non-magnetic variety β, the transformation taking place about 320°.

6. Cobalt shows a transformation at about 1080°.

Similar examples can be given in the case of compounds; thus the carbide of iron, Fe_3C, shows a polymorphic transformation at 210° (Wologdine, Driesen, Honda and Tagaki, Chevenard).

In a mixture of two phases containing a pure metal or definite compound, the allotropic transformation, which occurs at a constant temperature, is shown on the diagram by an horizontal extending over the whole area in which the two phases can exist.

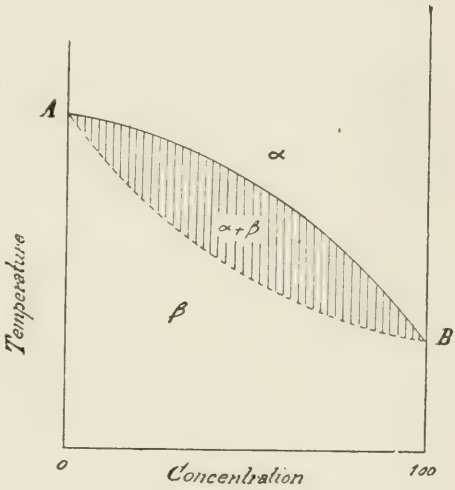


FIG. 45.

2. **Polymorphic Transformations in a Solid Solution.**—Each of the polymorphic varieties of a metal A is able to form a solid solution with a metal B, the solid solutions being non-miscible; the solid solutions can exist together at a given temperature in an exactly similar manner to a solid solution of two metals and a liquid solution of the two metals which may exist together in equilibrium as previously described. The change, from one solid solution to the other, takes place in accordance with laws which are identical, and is interpreted by two curves, showing the commencement and completion of transformation, which are analogous to the curves corresponding to the commencement and completion of solidification (Fig. 45). Internal polymorphic modification will take place in an alloy of two metals A and B over a range of temperature. For example, on cooling, during the given interval of temperature shown by the curves, the solid solution α will be converted into the solution β, and whilst this change is taking place the two solutions α and β will exist simultaneously and under equilibrium conditions, their respective compositions being given by the curves. The

curves may be of any of the three types previously described (Figs. 29, 31, and 32).

The existence of two phases on solidification is also possible, as previously described (eutectic and transition points); these solid solutions having definite chemical compositions at the temperature of complete solidification shown by the horizontal solidus (Figs. 35 and 38) may afterwards change in composition with change of temperature. Two curves of similar type to e_1f_1 and e_2f_2 (Fig. 46) give, in every case, the equilibrium compositions of the two solid solutions after they fall below the temperature, corresponding to the horizontal e_1e_2, at which the solid phases exist in equilibrium with the liquid phase at the transition or eutectic temperature (e_1 and e_2 compositions of the solid phases at this temperature). In practice, these lines e_1f_1 and e_2f_2 very closely approach the vertical and are therefore very difficult to determine, consequently many investigators assume them to be vertical to avoid the necessity of determining the respective points.

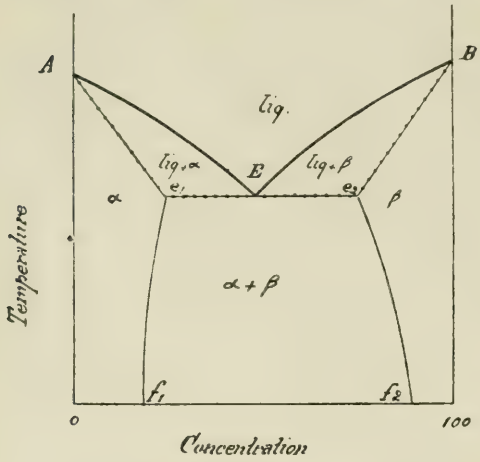


FIG. 46.

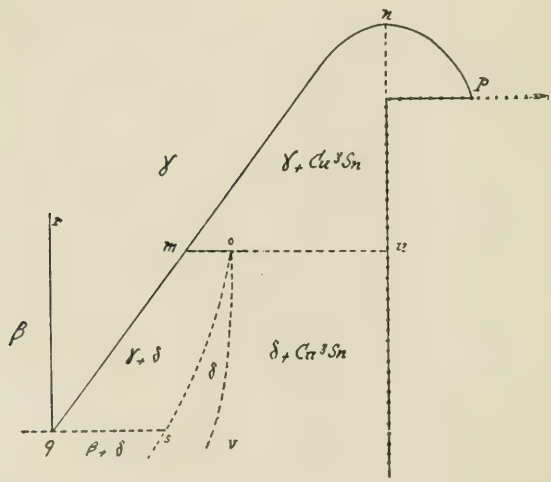


FIG. 47.

Obviously eutectic and transition points are also possible in the equilibrium curves in the solid state; in the former case the finely divided mixture separating along the horizontal line at the eutectic point being known as a *eutectoid*.

If further explanation of these phenomena is required it is only necessary to refer to what has been stated in the description of the solidification of alloys, replacing the word liquid by solid solution.

Example: With the copper-tin alloys, from the solid solution γ (Fig. 47) is formed a definite compound Cu_3Sn, which separates from this solid solution along the curve *mnp* having a maximum at a point *n* corresponding to the composition of the pure compound. This compound reacts at the temperature of the horizontal *uom* with the remaining solid solution γ of composition *m* to form another solid solution δ. Conditions similar to those of a transition point will be recognised, and the arrangement of the curves is the same as in that case. On the other side, the solid solution γ forms a solid solution β along the line *qr*, and the two curves *rq* and *mq*, separating γ from β and δ respectively, meet at a point *q* which is the eutectic point on the horizontal *qs* along which the eutectoid $\beta+\delta$ is formed.

This case illustrates the formation at a definite temperature, during cooling, of a solid solution δ at the expense of two phases; if δ were a compound, the lines *os* and *ov* would be vertical. This occurs in the solid state with the formation of Ni_4Sb at 677° in the nickel-antimony series.

Transformations with Reactions.—The transition and eutectic points already described are strictly speaking transformations accompanied by reactions, inasmuch as there is a formation or disappearance of a phase at the expense of two others of different chemical composition.

This fact will be illustrated in a later chapter in the case of steels (p. 131); at the transformation temperature 723° C., where the solid solution γ iron-carbon disappears on cooling with the formation of α iron and iron-carbide which occur as a eutectoid called pearlite.

The transformations occurring in solid alloys are determined by lines known as *transformation lines* or *critical lines* and the temperatures at which the verticals, corresponding to definite alloys, cut these lines are known as the *transformation temperatures* or the *critical points* of the respective alloys.

What has been stated with regard to the equilibrium of solid phases proves that if a metal A has a polymorphic or allotropic transformation point at a temperature T, the addition of a metal B may or may not vary this temperature according to whether the metal B is or is not miscible with the metal A in the solid state.

EQUILIBRIUM DIAGRAMS

The diagram, combining the melting point and solidification curves and the curves showing the transformations taking place in the solid state, and therefore giving the complete history of all the internal chemical modifications that occur during the solidification and cooling of binary alloys, according to their composition and temperature, is called an *equilibrium diagram*.

The problem as to the chemical composition of an alloy of two metals is now completely solved so long as the alloy is in a state of equilibrium and the temperature and average concentration of the alloy are known; the average concentration being the proportions of the two metals that the alloy contains. Particularly important is the fact that the chemical constitution at atmospheric temperature is known if the alloy is in equilibrium; this is the first information to help in the examination of the microscopic structure of alloys.

A short summary will now be given of the principles enunciated during the consideration of the various typical elementary cases that are met with in equilibrium diagrams and also a brief account of the experimental methods employed in their construction. The reader will then have a clear conception as to the construction of the equilibrium diagram, which is essential to the study of the microscopical constitution of alloys.

Interpretation of an Equilibrium Diagram of Two Metals.—It must be remembered, when considering the summary of the principles previously given, that the construction and interpretation of an equilibrium diagram requires both care and knowledge.

A. The lines constituting the diagram of a binary alloy divide it into several fields or equilibrium areas occupied by one or two phases: in the case of one phase, the chemical composition or concentration at each position is, under equilibrium conditions, the mean composition or concentration of the alloy; for the particles composing the alloy are then of the same chemical kind. When there are two phases present, the particles, which may be more or less intimately mixed, are of two chemical kinds of known chemical composition at any definite temperature. This is illustrated figuratively by the point M (Fig. 48) having as abscissæ the mean concentration of the alloy X and as ordinate a temperature T, horizontal FG; the abscissæ x_α and x_β of the points of intersection with the lines limiting the area of two phases in a lateral direction, give the concentrations of the two phases α and β existing together in equilibrium at a

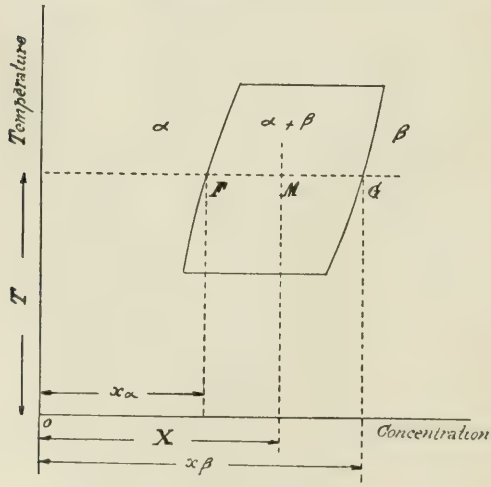


FIG. 48.

temperature T°. Further, the relative proportions of the two phases α and β are given by the equation

$$\frac{\alpha}{\beta} = \frac{MG}{MF}$$

It is seen that in the case of an area containing two phases and at any given temperature the quantity of each phase varies directly with the mean chemical composition X, and, moreover, all vertical lines on the diagram indicate the existence, in the adjacent sections, of a phase which remains of constant composition with change of temperature. This occurs when one of the phases is a definite chemical compound.

B. All horizontal lines on the diagram correspond to the simultaneous existence of three phases at this temperature, and consequently on passing through this temperature a reversible reaction occurs at a constant temperature. The compositions of the three phases is given by the abscissæ of the extremities of the horizontal line and by the intermediate point where the other lines of the diagram meet.

Let x_1, x_2, x_3 be the concentrations, arranged in their order of magnitude, of the three phases α_1, α_2, and α_3, then, at the temperature T of the horizontal, the following reaction occurs :

$$\alpha_2 \rightleftarrows \alpha_1 + \alpha_3$$

the phase α_2 can only exist on one side of the horizontal shown on the diagram.

C. On passing through an oblique line of the diagram there is an increase or decrease in the number of phases. In particular, below an inclined solidus there is only one phase, in other words, a solid solution.

D. When two lines of the diagram cut one another and form an angle between them, both lines being above the horizontal at the point of intersection, there is a simultaneous deposition of the two phases and the formation of a eutectic (known as a eutectoid if both the phases taking part in the reaction are solid) when the temperature falls and the horizontal line at the point of intersection is passed.

Construction of the Diagrams.—The passage through a line of the diagram is accompanied, in every case, by a change in all or some of the physical constants and properties of the alloy ; density, specific heat, electrical resistance, thermo-electric power, magnetic properties, etc.[1] Therefore, if the variation of one of these properties with change of temperature is studied, when one of the lines of the diagram is passed through a comparatively rapid change in the property under examination will be observed and will appear in

[1] This statement does not imply that these properties are only functions of the equilibrium diagram.

the curve, in which the respective property is plotted as a function of the time, as an irregularity in the general form. The temperatures at which these irregularities are found will correspond to the temperatures at which the lines of the diagram will meet the vertical lines corresponding to the compositions of the alloys examined.

The determination of cooling curves which will now be considered, the operation being known as *thermal analysis*, is merely a typical instance of this principle ; further, it may be stated that the method of thermal analysis is almost exclusively employed for the determination of melting point and solidification curves because of the comparatively large heat evolutions occurring under these conditions. For the identification of the transformation points in the solid state dilatometric and magnetic determinations are both employed, and in some cases the alterations in thermo-electric power and electrical resistance are also measured.

It must not be overlooked that with any given transformation there may be well-marked alterations in certain of the physical properties whilst others remain practically unchanged ; for instance, the melting points of lead and tin are clearly shown by thermal analysis and the change in electrical resistance (de la Rive), but there is no corresponding change in the thermo-electric power (Cermak and Schmidt) ; the nickel transformation point in the solid state, very difficult to observe by the dilatation method, is easily found from the thermal analysis and also from the study of the magnetic properties of the metal: the zinc transformation point, found to occur at 360° by the electrical resistance method (H. Le Chatelier), is not observable by thermal analysis ; the separation of two non-miscible liquids from the melted alloys of lead and zinc, accompanied by an inappreciable liberation of heat, is clearly shown by the change in electrical resistance (Bornemann and Muller). The reversible transformation point of white tin to grey tin has been determined by the measurement of the electromotive force.

The accuracy of these determinations will obviously depend on the amplitude of the variations and the sensitivity of the methods and apparatus used in their measurement, and it is therefore essential to employ every available means in the scientific study of the chemical equilibrium of two metals. Under ordinary practical working conditions the following methods are employed :—

1. Thermal analysis for melting points and transformation temperatures.

2. Dilatometric and magnetic methods for the transformations occurring in steels.

A short description of the method known as *thermal analysis* will now be given, this being the method in most general use at the present time.

Thermal Analysis.—The relationship between the slope or direction of the cooling curves and the equilibrium diagrams has been shown during the examination of the various simple typical cases met with in these diagrams. By cooling curves are meant the curves having as a function of the time, the temperature of an alloy which is allowed to cool in such a manner that it is protected or insulated from all external sources of heat capable of affecting the uniform rate of cooling. Under these conditions any irregularities in the curves must be due to internal liberations of heat caused by modifications in the chemical constitution of the alloys.

These irregularities may be divided into two main classes:

1. Break or change of direction in the curve corresponding to the passage through an inclined line of the diagram (points *b* and *c*, Fig. 30, p. 33; also Figs. 34, 35, pp. 35, 39).

2. Arrest or horizontal section of the curve denoting an isothermal reaction between three phases, corresponding to the passage through a horizontal line of the diagram. This case also occurs with two phases when they are of the same composition; for example, the common points of liquidus and solidus in the case of pure metals and the maximum of the liquidus (example: arrest *bc*, Fig. 27, p. 27).

Cooling curves are determined by taking readings of the temperature over definite intervals of time or by means of automatic recording appliances which plot the curves direct.

Low temperatures may be measured by means of ordinary thermometers, but for high temperatures thermo-couples or other suitable forms of pyrometer must be used; thermo-couples are nearly always used in the autographic recording appliances. With couples of platinum—platinum-rhodium (10 per cent. Rh) temperatures up to 1600° C. may be measured, but up to temperatures of 800° C. couples of copper-nickel or iron-constantan may be used, and will give a greater sensitivity and be far less expensive.

It is impossible in the present work to give the experimental details, types of apparatus, and the various precautions to be taken in the operations of thermal analysis, and only a brief description of the methods employed will be attempted.

1. To determine the complete cooling curve of an alloy the junction of the thermo-couple, suitably protected from the effects of the liquid alloy and the metallic vapour it evolves, is inserted into the alloy; the two wires of the couple being insulated from each other by any suitable means, except at the junction. The protection from the alloy is effected by tubes, closed at one end, made of any refractory material, which is impermeable and is not attacked by the liquid bath, such as porcelain, fused silica, fireclay, or even

magnesia in the case of metals which readily form silicates. The insulation is effected by means of refractories which are also insulators; the wires may be wrapped in asbestos, or one of the wires may be placed in a small tube of fireclay, porcelain, or fused silica.

2. The couples must be frequently calibrated by checking or comparison with a series of known temperatures: boiling points of water, 100°; naphthaline, 218°; sulphur, 444·6°; melting points of tin, 231·8°; antimony, 630°; silver, 960·5°; gold, 1063°.[1]

3. The autographic recording apparatus actually in use consists of a mirror galvanometer, the spot of light from which is received on a sensitive photographic plate or paper. The horizontal deflections of the spot of light are proportional to the temperature and the photographic surface is moved in a vertical direction at uniform speed by clockwork. Typical forms of this apparatus are those designed by Kournakow, Coste, Rengade, etc.

Variations in the Method of Thermal Analysis.—Instead of plotting cooling curves of the ordinary type which are simple time-temperature curves $t=f(z)$ (t=temperature; z=time), one of the several derived curves may be plotted.

1. Osmond, in determining the critical temperatures of iron and steels, constructed cooling curves having the temperatures as abscissæ, and the number of seconds the alloy took to fall through a given interval of temperature as ordinates. This curve gives, within limits, the inverse of the rate of cooling as a function of the temperature—*inverse rate curve.*

2. With the object of minimising the effects due to possible irregularities in the rate of heating and cooling, especially in cases where the evolution or absorption of heat at the critical temperatures is very slight (frequently the case in transformations occurring in the solid state), Roberts Austen introduced the differential method of compensation.

The temperature of the sample under examination and the difference in temperature between the sample and a neutral body, placed as near as possible to the sample, are measured simultaneously. The neutral body must be heated and cooled under identical conditions to the sample and must not present any discontinuity of thermal properties (transformation points, etc.) within the range to be observed. The curve is plotted showing this difference of temperature as a function of the temperature of the specimen under examination. Any variation of the internal heat of the specimen examined alters the difference of temperature between the specimens, and appears as an irregularity on the curve. This method can only be

[1] Translator's note: Melting points of lead, 327°; zinc, 419°; aluminium, 659°; pure sodium chloride, 800°; copper under charcoal, 1084°.

conveniently used for solid alloys. The autographic recording of such curves has been accomplished by means of the Saladin double galvanometer, which has been successively perfected by Le Chatelier and Broniewski. This method may be made completely automatic as described by one of the authors.[1]

3. Curves showing the rate of cooling as a function of the temperature may be plotted direct; to do this the rate of cooling at any instant is measured by means of Dejean's galvano-meter. By combining this apparatus with the double galvanometer the curves may be autographically recorded.

It is not possible, in the present instance, to consider in detail the curves plotted by these various methods, and reference should be made to one of the many text-books of thermal analysis.[2]

It has been shown that it is possible to study and record variations in all physical properties, as functions of the temperature, for any given composition and to note the irregularities corresponding to the passage through the lines of the diagram. Recourse may also be made to the variations in specific density (p. 63), electrical resistance (p. 59), thermo-electric power (p. 62), magnetic properties (p. 65). Later it will be shown how the examination of the micro-structure of quenched alloys helps to complete this information.

Instead of taking a fixed composition and examining the variations and physical properties with change of temperature, in other words, examining the changes occurring along a vertical line of the diagram of known abscissæ value, the variation in the properties of alloys of different concentrations at a fixed temperature may be examined, this being the inverse case in which the ordinate is a constant and the abscissæ variable. The points of intersection between the horizontal line under examination and the lines of the diagram are marked by sharp changes in the direction of the curve showing variations in the physical properties with change of composition at this temperature.[3]

This method is only practically applicable when the temperature chosen at which the complete series of experiments can be made is

[1] Portevin, "Notes sur le galvanomètre differentiel" (*Revue de Mét.*, vol. v. p. 295, 1908).

[2] Rengade, *Analyse Thermique*, Paris, Hachette, 1909. Portevin, "La méthode d'analyse thermique du professeur Tammann" (*Revue de Mét.*, vol. iv. p. 797, 1907). "Notes sur l'emploi du galvanomètre double" (*Revue de Mét.*, vol. v. p. 295, 1908). "Remarques sur les courbes différentielles dérivées" (*Revue de Mét.*, vol. vi. p. 1358, 1909).

[3] Tammann's method of thermal analysis, based on the study of the duration of the eutectic arrest in each alloy of the series as a function of the composition is indirectly included here since it only applies to isothermal reactions, namely, the horizontal lines of the diagram corresponding to the simultaneous existence of three phases.

the atmospheric temperature, so it should therefore be considered as a means of confirming the diagram indicated by the other method, and as the final confirmation that the constitution of the alloy, in a state of equilibrium at ordinary temperatures, is as indicated by the diagram ; this verification of the final state of equilibrium is extremely important.

The examination of the micro-structure of the alloys should always be carried out ; this subject will be considered later, when dealing with the relation between the diagram and microscopic constitution of the alloys.

The relation between the physical properties of the alloys and the equilibrium diagrams will now be briefly indicated in the case of alloys in *chemical equilibrium.*

It must be borne in mind that the diagrams are based on observations of variations in the physical properties of the alloys in the various systems occurring either with change of temperature or change of composition (changes occurring along vertical or horizontal lines of the diagrams) ; consequently, it may be generally stated that the physical properties of alloys may be studied by two methods :—

1. *By examining the variations in the physical properties of alloys of definite composition with change of temperature.*—No further description of this method is required, as it has been fully dealt with in describing the methods employed in the construction of the diagrams, the alloys being in a state of equilibrium. It will be necessary to return to this subject when dealing with alloys that are not in a state of equilibrium and with the displacement of the critical points.

2. *By examining the variations in the physical properties of alloys of varying compositions at a constant temperature, generally atmospheric temperature.*—It will be recalled that the maximum number of phases that can exist in an alloy of two metals at various temperatures is two (Phase Rule). Consequently, in the examination of a series of alloys of increasing richness in one of the metals, ranges of composition will be passed through having alternatively one or two phases, and the region containing only one phase may be so small that it may be reduced practically to a point (case of a compound non-miscible in the solid state at ordinary temperatures). To ensure that this point has been made absolutely clear, the three possible cases of an alloy of two metals A and B will again be considered.

(1) *Complete miscibility in the solid state.*—The alloys consist of a single solid solution, the concentration of which is the same as that of the alloy.

(2) *Complete non-miscibility in the solid state.*—The alloys consist

of the two solid phases A and B (unevenly distributed throughout the mass), and the relation between the phases $\frac{A}{B}$ is directly proportional to the concentration B per cent. of the alloy.

(3) *Partial miscibility in the solid state.*—Solid solutions are formed in the regions adjacent to the pure metals, the respective solid solutions being α rich in A and β rich in B ; between these two regions will be a third consisting of the two phases α_1 and β_1, each of fixed composition, α_1 being at the limit of saturation in the metal B and β_1 at the limit of saturation in the metal A at ordinary temperatures. Thus, there will be three regions :—

$$\alpha, \quad \alpha_1 + \beta_1, \quad \beta$$

In the mixture $\alpha_1 + \beta_1$, the relation $\frac{\beta_1}{\alpha_1}$ will be directly proportional to the total concentrations of the alloy.

In the case of an intermediate solid solution γ, there will exist in succession :

$$\alpha, \quad \alpha_1 + \gamma_1, \quad \gamma, \quad \gamma_1 + \beta_1, \quad \beta$$

If the solid solution is a definite compound

$$\alpha, \quad \alpha_1 + C \quad (C), \quad C + \beta_1, \quad \beta$$

in this case, the region "pure C" is reduced to a point.

Systems of this type may be considered, for the purpose of defining their equilibrium constitutions at ordinary temperatures, as being formed successively from two binary systems, the first consisting of the metal A and the compound C, the second of the compound C and the metal B. These two sub-divisions may then be classified into one of the three types previously described.

Conductivity and Specific Resistance.—With the object of avoiding complications in dealing with the relationship of these factors to the equilibrium diagram, the specific resistance ρ or its inverse, the specific conductivity $\chi = \frac{1}{\rho}$ will be chosen in the various examples described ; the conversion of one factor to the other can be easily made when required.

1. *Variations with change of composition.* The composition will be defined as the percentage by *volume* of one of the constituent metals, B for example, the specific conductivity being the conductivity per unit volume. The following laws enunciated by Le Chatelier have been completed and further developed by Guertler and by Kournakow and Zemczuznyj.

(*a*) *Complete miscibility of the two metals A and B in the solid state.*—The curve connecting the conductivity with the composition by volume takes the form Type I. (Fig. 49). There is a rapid fall in the conductivity on leaving the pure metals A and B, and the

existence of a point of minimum conductivity which is frequently very low compared to the conductivities of the pure metals A and B.

(*b*) *Complete non-miscibility of the two metals A and B in the solid state.*—In this case of a simple mixture of the two metals A and B, the conductivity is a linear function of the concentration (Type II. Fig. 49).

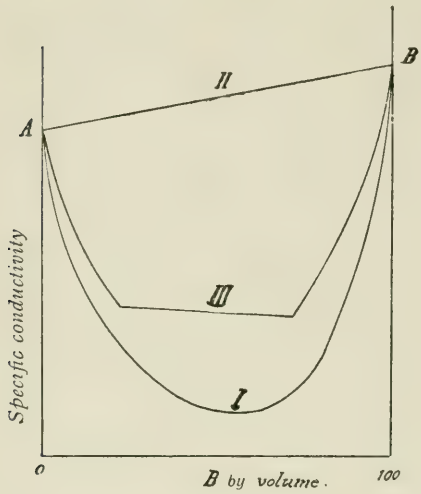


FIG. 49.

(*c*) *Partial miscibility in the solid state.*—The form of the curve can be deduced from the two previous examples (Type III.). The curve takes the form of Type I. in the regions of the single solid solutions α and β and Type II. in the intermediate area, consisting of a mixture of the saturated solid solutions α_1 and β_1.

The well-defined breaks in the curve render this method very valuable for finding the limits of the solid solutions α_1 and β_1 especially where the compositions of these solid solutions approach very closely the compositions of the pure metals, as, in this case, thermal analysis gives very unreliable results.

In all three cases considered the conductivity is always less than that of either of the pure metals.

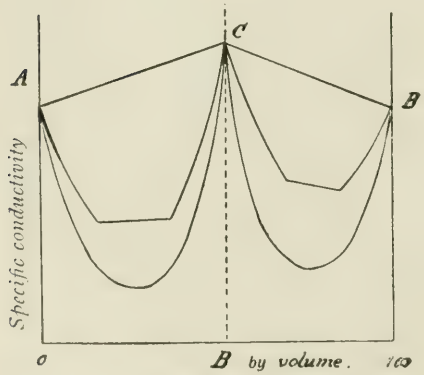


FIG. 50.

(*d*) *Case of a definite intermediate compound* C.—As previously stated, in this instance it is more convenient to consider the alloys in two series, the first, the metal A and the compound C; the second, the compound C and the metal B. In each series, according to the mutual solubility of A in C and C in B, the curves will be of one of the three types I., II., III.

It will be seen that when the compound C is miscible in the solid state, the composition of the compound is very well defined (Fig. 50). This fact is very useful for confirming the existence of a solid solution and for determining the composition of the compound. Further, it may be stated, that

rarely is the conductivity of an alloy, containing a compound, greater than that of either of the constituent metals.

2. Variations with Change of Temperature. — The temperature coefficient of the conductivity between 0° and 100° C. is given by the expression :

$$100 \frac{\chi_0 - \chi_{100}}{\chi_0}$$

χ_0 and χ_{100} being the specific conductivities at 0° and 100° C.

Guertler has shown that the variations of this coefficient with change of concentration obey the same laws as those already enunciated in the case of electrical conductivity, but without the respective values being strictly proportional or the curves identical. This coefficient may, therefore, be used in a similar manner to the conductivity for the verification of the diagram, but offers the great advantage that it is independent of the shape, size, and various local defects (cracks, flaws, inclusions, blow-holes, etc.) of the sample from the alloy.

It has already been stated, that the passage through the various transformation points is accompanied by very rapid changes in the conductivity and electrical resistance of the alloy and that these changes are sufficiently clearly defined to enable the transformation temperatures to be determined by this means. Transformations in the following systems have been determined by these methods : steels (Boudouard), brasses (Le Chatelier), aluminium bronzes (Le Chatelier, Barrée, Broniewske), German silver and zinc (Le Chatelier).

For the pure metals possessing no transformation points, the increase of resistance with temperature is proportional to the absolute temperature of the metal ($T = t + 273$).[1]

This relation does not hold good for solid solutions, the temperature coefficients are greatly diminished. Very interesting conclusions, from an industrial standpoint, may be drawn from the relation between the electrical conductivity and the equilibrium diagram.

1. Definite compounds being of no practical utility owing to their brittleness (this matter will be dealt with at a later period), recourse must be made to the pure metals whenever high conductivity is required. The metals must be purified with great care in order to eliminate the last traces of impurities—this being especially the case when these impurities form solid solutions, and therefore greatly reduce the conductivity when present.

2. Inversely, whenever alloys of high resistance or possessing comparatively constant resistance with change of temperature

[1] Consequently, all the pure metals have the same temperature coefficient, the only exceptions being iron, nickel, and cobalt.

are required, those consisting of solid solutions of concentration giving the minimum conductivity should be selected, as in Type I. Examples : Constantan 60 Cu + 40 Ni, cupro-manganese, etc.

THERMO-ELECTRICITY

1. **Variations with Change of Temperature.**—The curve representing the thermo-electric power as a function of the temperature may take one of the following forms (Broniewski) :

(1) In the case of a solid solution, the curve takes the form of a section of an hyperbola with the concave surface towards the top or bottom of the diagram.

(2) In the case of a mixture of two phases the curve is practically a straight line. The curves representing the thermo-electric power are, therefore, analogous to the conductivity curves, but are more complicated ; the chief difference arises from the fact that the thermo-electric power may have a positive or negative value, whereas the conductivity is always positive. It is owing to this difference that the definite compounds forming solid solutions which, in the conductivity curves, are represented by peaks in the curve, may be represented as maxima or minima in the thermo-electric power curves or even as an S-shaped branch marked by no discontinuity.

2. **Variations with Change of Composition.**—The curves giving, as a function of the volume composition, the variations of the thermo-electric power with change of temperature are similar but not identical to the thermo-electric power curves, as the branches of the curves representing solid solutions do not always point in the same direction in both cases (Broniewski).

The discontinuity of the thermo-electric properties at the transformation temperatures has been utilised to determine these temperatures. Examples : nickel steels (Boudouard), aluminium-copper alloys (Broniewski).

An extremely simple method of utilising the thermo-electric properties for the determination of the transformation points is due to Le Chatelier. At the two ends of a small cylinder of metal are fixed or welded the ends of two platinum wires, the other ends of which are connected to a galvanometer. Owing to the unequal heating of the specimen, one end of the cylinder commences to transform before the other end, the point or area of contact between the two varieties of the metal constituting a true thermo-electric junction which gives rise to an E.M.F. This fact, combined with the variation in resistance of the mass, causes a deflection of the galvanometer and determines the temperature of transformation.

Inversely, the passage from the solid to the liquid state may not be accompanied by any change in the thermo-electric power. Example : lead, tin (Cermak and Schmidt).

ELECTROLYTIC POTENTIAL

The electrolytic potential is the E.M.F. produced in an alloy of two metals, A and B, when placed in a cell made up as follows:

alloy/electrolyte/metal A

the electrolyte being a solution containing the ion A, or in other words, a salt of the metal A.

1. **Variations with Change of Composition.**—(*a*) *A single phase:* the E.M.F. varies regularly as a function of the composition and is therefore represented by a curve.

(*b*) *Mixture of two phases:* the E.M.F. remains constant and equal to that of one of the phases; it is represented by an horizontal line with a rapid change in direction at one end when it joins the E.M.F. curve of the other phase. It is obvious that the E.M.F. method of investigation gives a sharp change in direction of the curve in the case of a compound which is not soluble, whilst the electric conductivity and thermo-electric power curves clearly indicate definite compounds forming solid solutions. The two methods together, therefore, complete the information regarding the compounds existing in a system.

It must be stated that the electrolytic potential is not solely dependent on the alloy examined, but depends also on the nature and composition of the cell (electrolyte and less positive metal employed as the other element of the cell) and the duration of the experiment. Its measurement is, therefore, less accurate than the measurements of the other electrical properties.

2. **Variation with Change of Temperature.**—The variation of electrolytic potential with change of temperature has received very little consideration in the case of alloys. It was by this method that the equilibrium temperature for the transformation of white tin to grey tin was determined (Cohen). If the two modifications are taken as electrodes in an electrolyte of stannous chloride, the E.M.F. is reduced to zero at the transformation temperature.

EXPANSION, CONTRACTION, SPECIFIC GRAVITY AND DENSITY

The expansion and density will be considered together; the coefficient of cubical expansion being known, the variations per unit length and volume are known, and therefore the specific gravity and density. Contraction is merely a special case of a change in volume.

These factors being functions of each other, the most convenient factor will be chosen for each experiment; the expansion will be measured when the temperature is the variable; the specific gravity or density will be taken when the composition is the variable.

1. **Variations with Change in Temperature.**—As already stated, the study of the variation in volume of an alloy lends itself very readily to the determination of the transformation temperatures. This method possesses advantages as compared with the cooling curve method since the rate of cooling has no effect on the accuracy or sensitivity of the observations; also, the changes occurring over very small ranges of temperature can be examined, and therefore it is possible to make observations at temperatures as close as possible to the transformation temperatures. This advantage, however, is not solely confined to the expansion method.

The expansion or change in volume method has been used with success for the determination of the transformation points in steels, especially when the changes occur at low temperatures.

The changes in volume occurring during solidification vary considerably in different cases. In the case of the pure metals there is usually a contraction on passing from the liquid to the solid state. However, with certain metals such as bismuth, antimony, calcium, expansion occurs. This is also the case, according to Turner and Murray, with zinc and aluminium. According to the same authors the maximum and minimum expansion, in the copper-zinc series, corresponds respectively to the maximum and minimum distances existing between the solidus and liquidus shown in the equilibrium diagram. On the other hand, Ewen and Turner have found the maximum expansion to correspond to the pure eutectic in the cases of the lead-antimony and aluminium-zinc series.

With pure metals Carnilley states that the coefficient of expansion increases as the melting point of the metal decreases, and according to Broniewski the following equation:

$$\frac{\alpha_t}{F + T} = \text{constant}$$

is applicable in the case of the non-atomic metals (α_t = coefficient of cubical expansion, F = melting point, absolute temperature; T = temperature of the metal, absolute).

On passing through a transformation point in the diagram, the accompanying change in volume of different alloys indicates the amount of the respective phases present in a similar manner to the varying arrest times with the cooling curves. The transformation, on heating, may be accompanied by a distinct contraction or an arrest in the expansion; the very low coefficient of expansion of certain alloys at ordinary temperatures (*e.g.* Invar) is explained in this manner.

2. **Variation with Change of Composition.**—The change in volume is found from the alteration in specific gravity or density of the alloy. In the case of a mixture of two constituents, the specific gravity

varies directly as a function of the composition, and may therefore be easily calculated. In the case of a solid solution the specific gravity, as a function of the composition, is represented by a curve, the curvature of which is very slight and may be frequently neglected—the curve being taken as a straight line and the previous case applied. Sharp changes of direction in these curves only occur in the case of definite compounds, the formation of which is accompanied by definite changes in volume. (Example: FeSb, Cu_3Sn.) Maey has identified four definite compounds in the sodium-amalgam series by the observation of the specific gravity composition curves. Frilley has investigated the variations in specific gravity of the alloys of silicon with manganese, chromium, nickel, iron, tungsten, copper, and the alloys of the copper-aluminium, copper-cadmium, mercury-cadmium, and copper-tin series. He found a series of lines with points of intersection indicating definite compounds.

Inversely, the density curve is formed of segments of hyperbolas forming tangents to each other in the case of rapid changes in volume.

The breaks in the composition-specific gravity curves are often so small that they are imperceptible; moreover, there are sometimes maxima or minima which do not correspond to definite compounds (silver-tin, lead-bismuth series). The specific gravity and density are constants which present great difficulties in their accurate determination owing to the effect of cavities, inclusions, flaws, or work hardness in the cases where filings or turnings are used.

MAGNETIC PROPERTIES

The detailed description of the examination of the magnetic properties of alloys is too complicated to be dealt with in this work; these properties are greatly affected by various mechanical operations, hammering, vibration, shock, bending, etc., and will be very briefly considered.

1. **Effect of Variations in Composition.**—The following metals and alloys are strongly magnetic or so-called ferro-magnetic: iron, nickel, and cobalt, and certain alloys, investigated by Heusler, composed of slightly magnetic elements. The latter alloys consist of the slightly magnetic alloys of copper and manganese, to which have been added various elements such as Al, Sn, Sb, Bi and even As and Bo; the alloys exhibiting the strongest magnetic properties have the general formula $Al_xMn_yCu_{3x-y}$.

The binary compounds formed by ferro-magnetic metals with other metals are nearly all magnetic.[1] In the case of solid solutions formed by ferro-magnetic metals with other metals, those rich in

[1] Inversely, the compounds of ferro-magnetic metals with certain metalloids are non-magnetic. Examples: Co_5As_2, Fe_3P, Fe_2P, Fe_2S, Fe_4O_3. (Honda.)

the ferro-magnetic metal are usually magnetic, and those rich in the other metals are usually non-magnetic.

The ferro-magnetic metals, iron, nickel, and cobalt, exist in the non-magnetic state at high temperatures; the magnetic transformation temperature of any of the three metals is lowered by the addition of either or both of the remaining metals. The alloys of these metals may be magnetic or non-magnetic according to whether one or more of the metals is present in the magnetic state, or both are present in the non-magnetic condition. The investigation of the iron-nickel, nickel-cobalt, cobalt-iron alloys by Weiss has indicated the existence of the compounds Fe_2Ni and Fe_2Co, by the discontinuity, observed in the variations of Curie's constant, at concentrations corresponding to these compounds.[1] The investigation of the slightly magnetic alloys, antimony-silver, lead-tin, zinc-aluminum, by E. L. Dupuy,[2] has shown that the magnetic properties vary directly with the composition in the case of a simple mixture of the two constituents; definite compounds behave as bodies possessing definite magnetic properties of their own; while the variations in magnetic properties in the case of solid solutions may be represented by a curve.

2. **Effect of Change of Temperature.**—In the case of the ferro-magnetic metals, certain transformations are accompanied by a sudden loss of magnetic properties, indicating magnetic transformation temperatures; with iron, this change is progressive, and is known as the A_2 point; with nickel it occurs about 320° and with cobalt about 1080°. In the magnetic alloys of these three metals, the magnetic transformation temperature varies with the composition according to the transformation line of the equilibrium diagram (examples: iron-carbon, iron-nickel). With steels, the magnetic properties again offer an accurate and easy method of determining the transformation temperatures. The magnetic properties of Heusler's magnetic compound alloys disappear between 60° and 350°, according to the composition of the alloy; the effect of temperature in this instance is extremely complex.

Other physical properties of alloys could be equally well studied either independently or as functions of those already investigated, such as the heat of formation, the specific heat, thermal conductivity, optical properties, sonorous properties, heat of solution, etc.; but the relation between these properties and the equilibrium diagram has either been very little studied or has given unreliable information. The connection between the equilibrium diagram

[1] Curie's Law: If θ is the magnetic transformation temperature (disappearance of magnetic properties), the coefficient of magnetism χ above θ is given as a function of the absolute temperature T by the equation $\theta = \chi(T - C)$, where C = Curie's constant.

[2] *C. R.*, vol. 158, p. 793, 1914.

and the micro-structure of the alloys will now be described and also the relation to the physical properties of the alloys. It will be remembered that, in dealing with the equilibrium diagrams, only alloys in a state of equilibrium were considered ; therefore, it will be possible to examine only those alloys in equilibrium at ordinary temperature—the examination at higher temperatures has been attempted in a few isolated cases, but it is accompanied by great experimental difficulties as it is necessary to work *in vacuo* to protect the surface of the specimen from oxidation (Oberhoffer).

RELATION BETWEEN THE MICRO-STRUCTURE AND THE EQUILIBRIUM DIAGRAM

Physical Constitution of Alloys in Chemical Equilibrium

It has been shown that the construction of the equilibrium diagram has completely solved the problem, mentioned at the commencement of this chapter, in those cases where physico-chemical equilibrium is attained, *i.e.*, the determination of the chemical composition of the constituents of an alloy which are seen by microscopical examination. It has been found that, at ordinary temperatures, all the particles may belong either to one phase and have the same chemical composition, which will be in this case the percentage composition of the alloy, or belong to two phases of definite chemical composition—the proportion of each phase present being known. The microscopical constitution of these two cases will be considered in this order. On the other hand, the equilibrium diagram supplies no information as to the structure of the phase, or any part of the phase ; neither does it give any conception as to the form, size, and distribution of the particles in the case of a mixture of two phases ; this information will be supplied by microscopical examination.

A. Case of a Single Phase (Pure Metal, Homogeneous Solid Solution, Pure Compound)

If a polished specimen is etched with a suitable reagent, and examined under the microscope, there will be seen a network of lines dividing the surface into a number of approximately polygonal grains (Fig. 51, Pl. III., p. 68). If the etchant operates by dissolving the metal, on further etching certain grains will be found to dissolve more readily than others, indicating varying solubility in the reagent (Figs. 55–58, Pl. IV., p. 69) ; by this treatment there are formed a number of facets of varying brilliancy, according to the direction of the light reflected by the surfaces. On continuing the etching or by using other reagents, these facets are corroded, and give place to a large number of small geometric figures which, on any one facet, are all identical in shape, these are known as *etching pits*

or *etching figures*, and are identical to those found on the faces or sections of crystals; these etching figures are visible under high magnification (Fig. 53, Pl. III.). If the reagent operates by oxidation, forming films on the polished surface of the specimen of varying colour according to their thickness, the coloration of the various grains will be different (Fig. 52, Pl. III.; Fig. 59, Pl. IV.; Figs. 67–71, Pl. VI., p. 72); indicating different rates of oxidation of the various grains.

Each facet represents a section through a crystal or "grain" in the plane of the polished surface; these grains are of identical chemical composition, since, by hypothesis, they belong to a single phase. Each grain is a crystal, in other words, a homogeneous mass of crystallised matter having its own orientation. A crystal is anisotropic, in other words, its properties vary in different directions but are the same in any given direction in all cases; therefore, the mass of crystal grains of varying orientation, when cut through a single plane, as in the case of a polished surface, exhibit surfaces having varying properties which consequently behave differently when subjected to chemical attack.

Other properties peculiar to crystallised material will also be noted, such as twinning and cleavages due to deformation. Thus, if an alloy *partially polished* is subjected to a slight deformation, fine lines known as *slip bands* will appear on the polished surface. These *slip bands* will be parallel and equi-distant from one another in any single grain, but will vary in direction in different grains (Fig. 54, Pl. III.). Again, certain grains are often crossed by straight, parallel-sided bands of a different colour, brilliance, or appearance to the remainder of the grain, indicating the presence of *twinning*. Finally, any investigation to discover the commencement of fracture in a grain, often shows this rupture to occur across the grains by a series of plane surfaces. These surfaces correspond to *cleavage planes* of crystals, thus revealing a discontinuous vectorial property characteristic of crystallised matter. It has been found possible to perform all the above experiments with metals or alloys having very large grains and from which it has been able to isolate individual grains; but, in general, these grains are of very small dimensions and, in the mass, the inequalities of the various properties are exactly compensated by the varying orientation of the different grains. The mass may therefore be considered as isotropic.

The origin of these grains must now be considered. The solidification of a single phase will be chosen as an illustration. The commencement of crystallisation will be described, after which the changes that occur before passing into another equilibrium region will be dealt with, and finally those changes brought about by transformations without chemical modification or the formation of two phases.

DIFFERENTIATION BETWEEN CRYSTALS OF THE SAME PHASE.

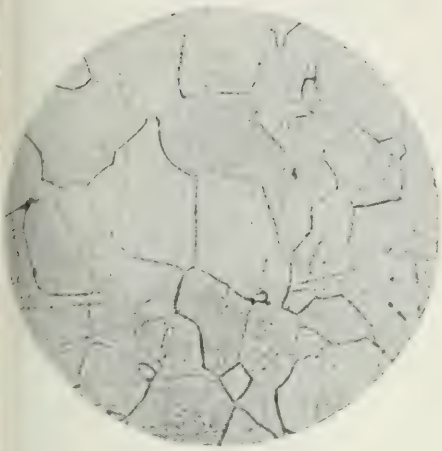


FIG. 51.—Electrolytic iron (annealed).
Etchant: Bénédicks' reagent.
(× 300.)

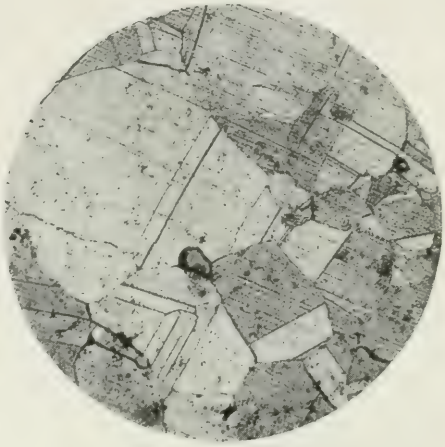


FIG. 52.—Arsenical copper.
Etchant: Ammonia.
(× 200.)

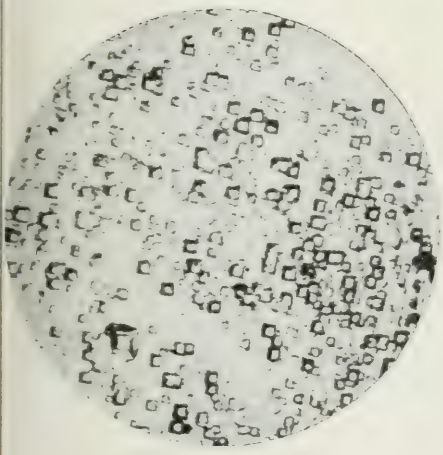


FIG. 53.—Etching figures on a single crystal face of iron.
Etchant: Copper ammonium chloride. (× 580.)

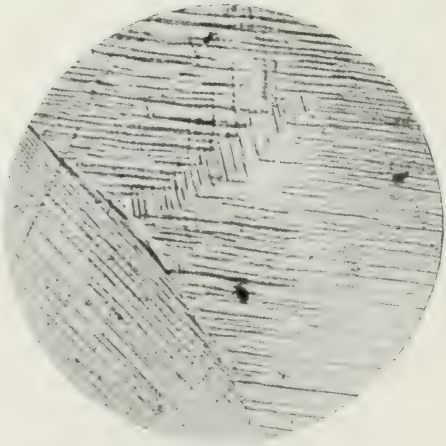


FIG. 54.—Copper tin alloy 5½% Sn, showing slip-bands.
(× 200.)

UNEQUAL SOLUBILITY OF DIFFERENT FACES OF SIMILAR CRYSTALS.

Progressive etching of electrolytic copper with nitric acid.

FIGS. 55-58.—Same field of view in each case.

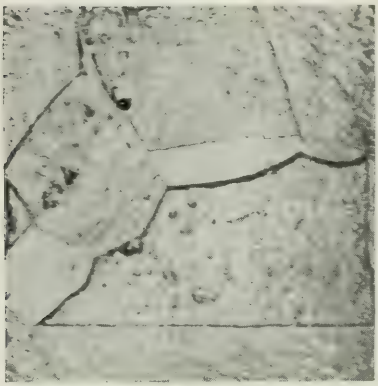


FIG. 55.

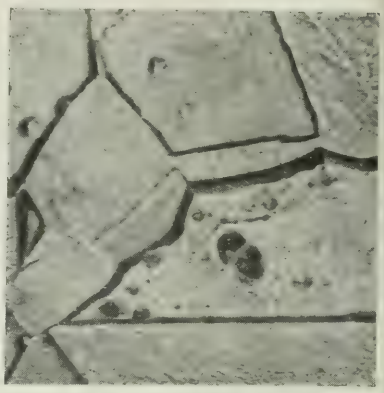


FIG. 56.

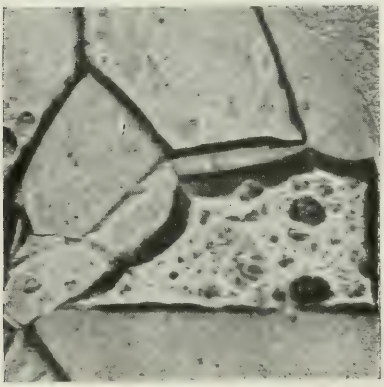


FIG. 57.

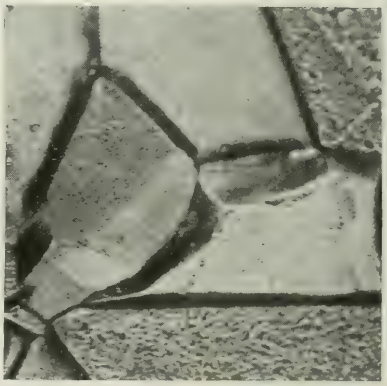


FIG. 58.

FIG. 59.—The same field etched with acid ferric chloride.

Solidification of a Single Phase—Crystal Grains.—At the commencement of solidification there are formed in the liquid small crystals of varying orientation or centres of crystallisation which develop as fast as the solidification proceeds. The development may take place by the growth of the plane faces of each crystal in the case of

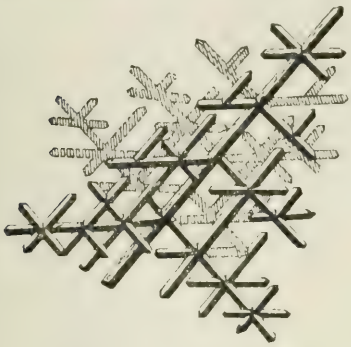


FIG. 60.—Outline of dendrite (Tschernoff).

FIG. 61.—Crystallite of cast-iron (Grignon, 1775).

definite chemical compounds or metallic compounds ; on the other hand, with pure metals and solid solutions the development nearly always occurs along the axes of an octahedron [1] forming tree-like structures known as *crystallites* or *dendrites*, the intermediate branches of which continue to increase in number until they fill the spaces between the main axes first formed. Figs. 60 and 61 illustrate the general outline of such a crystal which, if allowed to develop freely and at the same speed in all directions, would finally take the form of an octahedron. If, during solidification, the residual liquid is poured off to leave a network of crystalline material, or if the mass contracts owing to the contraction occurring during solidification, these dendritic crystals will be preserved and may be examined by fracturing the solidified metal. The classic examples described by Tschernoff (Fig. 63, Pl. V., p. 72) and Osmond were obtained in this manner. Dendrites are found in microscopical sections particularly in the cases of non-homogeneity of solid solutions or when two phases are present, both of which will be considered later.

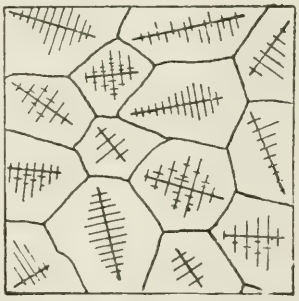


FIG. 62.—Crystallisation from centres (Desch).

The crystallites in the cases of pure metals and solid solutions continue to grow until finally all the liquid disappears ; each crystallite is limited in its growth by the adjoining crystallite, and the grains formed are, therefore, allotriomorphic crystals. The growth

[1] Most metals crystallise in the cubic system, the directions of the dendritic branches being the quaternary axes of the cube.

in different directions is very variable in these dendrites, and consequently the grains which they form are rarely equiaxial.

During the solidification of a metal in ingot form, crystal grains are first formed on the surface of the ingot, and crystallisation spreads from this surface; but lateral development is hindered by the adjacent grains, and the outer skin of the ingot, therefore, consists of parallel-sided grains elongated towards the centre of the ingot. This basaltic structure occurs in all chill-cast alloys to a varying depth, dependent on the composition of the alloy and the conditions of cooling (Figs. 64, 65, Pl. V., p. 72).

The number of grains in any given volume of an alloy depends on the number of centres of crystallisation formed during solidification. According to Tammann, the speed of spontaneous formation of centres of crystallisation (increase in the number of centres of crystallisation per unit of time per unit of mass), very low at the melting point, slowly increases as the temperature falls, whereas the linear speed of crystallisation from these centres is at a maximum at the melting point. Therefore, the number of grains increases as the speed of solidification increases, and large primary grains may be obtained by very slow solidification of the alloy.[1]

Other conditions being constant, the number of grains in an alloy is also dependent on its chemical composition, small quantities of foreign substances in particular being able to alter completely the number and, consequently, the size of the crystal grains of an alloy under given conditions. After solidification, the alloy is found to consist of a number of grains possessing no regular geometric form and each corresponding to an individual dendrite, and therefore possessing a constant crystalline orientation within the grain—the conditions of solidification having an influence on both the number and the distribution of these grains.[2]

Owing to the intermeshing of the dendrites in the partially liquid state, the outlines of the dendritic structures in the solid alloy frequently present a very irregular and jagged appearance. These joints or crystal edges, therefore, have no relation to the crystalline form of the phase considered.

[1] By this method one of the authors has been able to obtain grains sufficiently large to enable compression test-pieces to be made of a single grain.

[2] It is necessary to mention that the formation of dendrites may be facilitated by the addition of certain viscous substances or colloids to salts which ordinarily crystallise as regular crystals bounded by plane faces. Bowman, in this manner, has obtained all the intermediate forms between the ordinary crystals and the tree-like and radiating structures. By assuming an analogy in the case of metals, it is possible to imagine that the addition of even a small quantity of some foreign metal may cause the texture of the alloy to change from a crystalline to a fibrous character. The conditions of cooling also exert an influence on the crystalline texture: Osmond and Cartaud have shown that, by slow cooling, a solution of chrome alum will deposit violet octahedra, whereas, by rapid cooling, crystallites in the cubic system are formed; they have obtained these two forms simultaneously, side by side, in the same solution.

It is now possible to define the crystalline structure due to primary crystallisation, this being the structure of all single phases after solidification. It has been shown that the conditions of cooling affect the size and even the orientation (outside skin of chill-cast alloys) of the grains as well as the chemical constitution of the solid solution.

Numerous causes tend to modify or destroy this structure. Obviously the passage through a transformation line, which, in the case of solid solutions, indicates the formation of two phases, and with pure metals and compounds corresponds to the formation of a polymorphic modification, will both have this effect; but even without passing through any line of the equilibrium diagram and by merely remaining in the equilibrium area of the phase considered, the grains are modified by continued annealing, deformation, and by annealing after deformation. These respective cases will now be considered.

Modifications in the Structure of a Single Phase

Annealing.—By annealing is understood all heating of the specimen in the equilibrium area of its existing phase. This annealing causes the grains of the phase to grow in size; consequently, there is a diminution in the total number of grains—the small grains disappearing at the expense of the larger grains. This growth, in general, increases with rise of temperature (Figs. 66–71, Pl. VI. and Fig. 72, Pl. VII., p. 72); the growth also depends on the amount of previous cold-work to which the alloy has been subjected.

Cold-work and annealing subsequent to cold-working.—By cold-work is understood the operation of permanently deforming metals and alloys and thereby causing certain modifications in their properties due to internal strains within the material.

The effect of cold-work produced by any given deformation diminishes as the temperature is raised to that at which the deformation was effected. Cold-work deforms, changes the orientation, splits up, and finally destroys the crystal grains; it may also destroy the crystalline network of the grains. The polyhedral structure may be destroyed by continued cold-work.

Annealing causes the recrystallisation of the mass. This recrystallisation increases with increase of temperature and time.[1] The temperature at the commencement of recrystallization is lower as the amount of previous cold-work is greater. With certain metals (lead, tin, cadmium, zinc) recrystallisation has been observed to take place at ordinary temperatures (Fig. 73, Pl. VII., p. 72).

[1] This recrystallisation is sometimes termed secondary crystallisation to distinguish it from crystallisation occurring during solidification, known as primary crystallisation.

According to certain authorities (Ewing and Rosenhain), previous deformation is essential if recrystallisation is to occur on annealing; but it must not be overlooked, in considering this theory, that it is extremely difficult to avoid all deformation in a solid metal. Nearly all industrial metals are worked, forged, etc., after casting; moreover, internal stresses and deformation are produced in cast metals by the contractions, etc., which occur during cooling; finally, cold-work is done on the specimen during its preparation by sawing, filing, etc.

As shown later, quenching produces a similar effect to cold-work.

It is important to remember that the recrystallisation becomes greater as the cold-work or strain is more severe, and that the minimum annealing temperature is then higher and the time of anneal more prolonged.

Annealing after local deformation.—Charpy and Sauveur have shown, in the case of mild steel, that after local work (produced, for example, by a Brinell hardness test) an annealing about 650° C. causes considerable recrystallisation, the growth being at a maximum in the grains forming a ring round the impression of the ball (Fig. 75, Pl. VII.). According to Sauveur, the growth is at a maximum when the deformation has been caused by a stress slightly in excess of the elastic limit of the material.

The investigation of bent and re-flattened sheets shows the growth to commence at the beginning of the bend, and also the existence of an area consisting of exceptionally large grains (Humphrey, Robin).

Inversely, deformation of large grains followed by annealing will refine the structure into small grains (Portevin, Tinoféef) (Fig. 74, Pl. VII.).

Effect of a Polymorphic Transformation in a Metal or Definite Compound.—In the present instance only a single phase is being considered. Therefore, in dealing with polymorphic transformations only pure metals or definite compounds can be considered, as with solid solutions there exists an area consisting of two phases between the commencement and completion of the transformation (*see* p. 49). This case will be considered in due course (*see* p. 76).

When a polymorphic transformation occurs in a pure metal or definite compound, a single phase, α, exists before the transformation, and a single phase, β, after the transformation; the only structural evidence of the change is a crystalline modification of the grains.

Two cases are possible :—

1. After transformation, the grains are found to be of the same size; the grains of the new form β being to all appearances similar to those of the α variety. This is known as a direct transformation.

DENDRITES AND CRYSTALS.

Fig. 63.—Iron crystalite. (Tchernoff.)
(× $\frac{2}{5}$.)

Brass : 58 % Cu.

Macrographic sections of ingots as cast.

Etchant : Acid ferric chloride.
(× $\frac{1}{3}$.)

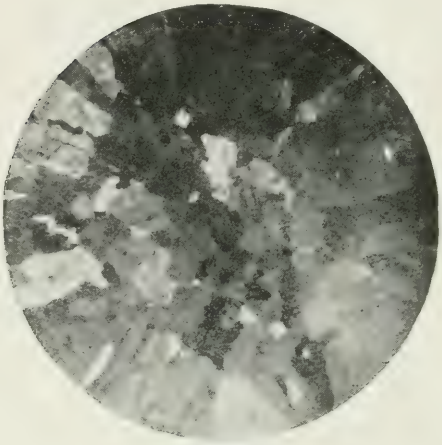


Fig. 64.—Sand cast.

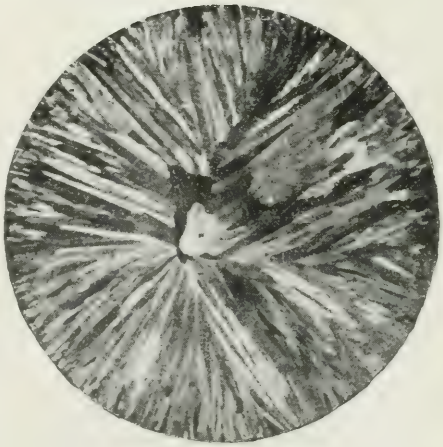


Fig. 65.—Chill cast.

GROWTH OF CRYSTAL GRAINS IN A SINGLE PHASE.

Figs. 66–73.—**The annealing of cold worked zinc.** (Timoféef.)

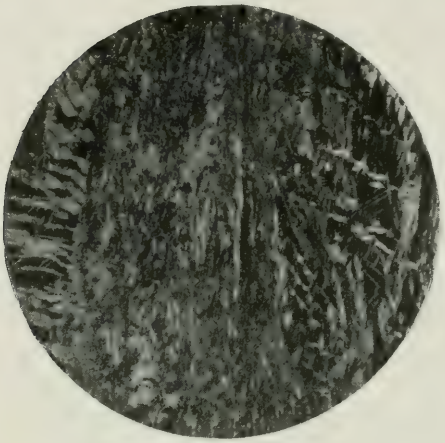


Fig. 66.—Cold worked in a press.

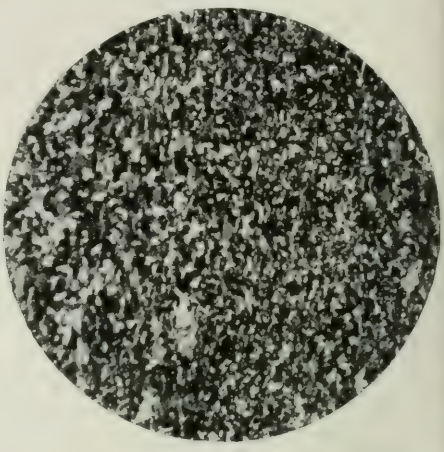


Fig. 67.—Annealed for 6 hours at 65° C.

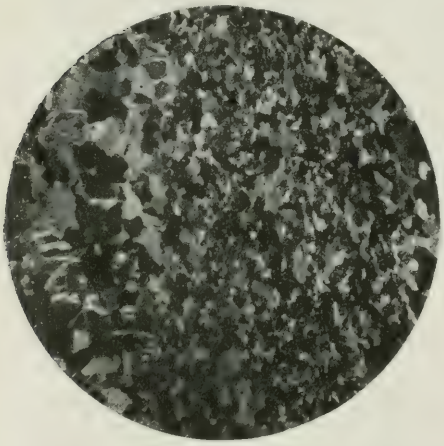


Fig. 68.—Annealed for 6 hours at 100° C.

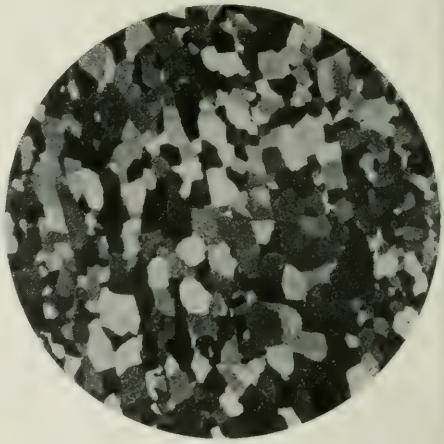


Fig. 69.—Annealed for 6 hours at 218° C.

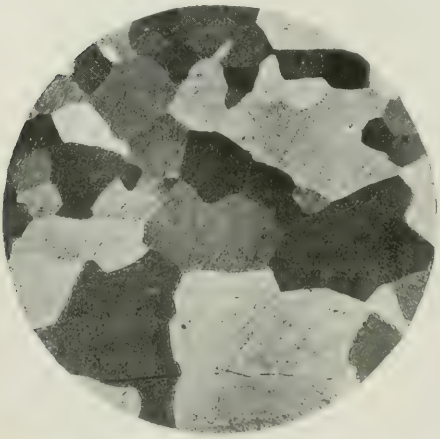


Fig. 70.—Annealed for 6 hours at 302° C.

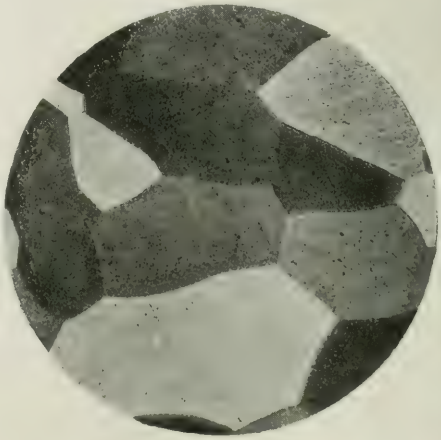


Fig. 71.—Annealed for 6 hours at 360° C

GROWTH OF CRYSTAL GRAINS IN A SINGLE PHASE *(cont.)*.

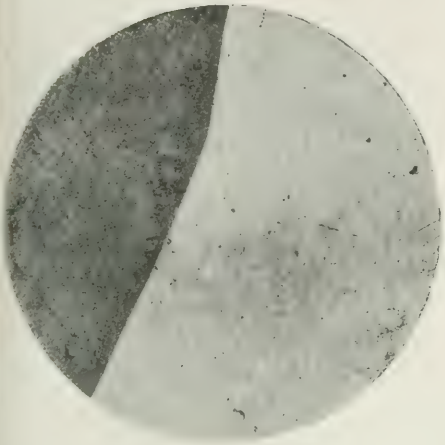


FIG. 72.—Annealed for 2 weeks at 302° C.

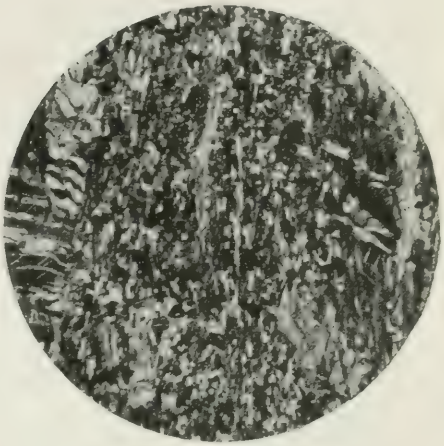


FIG. 73.—Recrystallization at ordinary temperatures (15 days).

RECRYSTALLIZATION EFFECTED BY ANNEALING AFTER LOCAL COLD-WORKING.

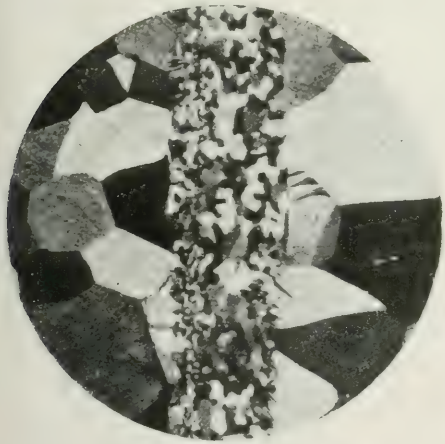


FIG. 74.—The effect on zinc of local cold work with a knife blade, followed by annealing at 100° C. (TIMOFÉEF.)

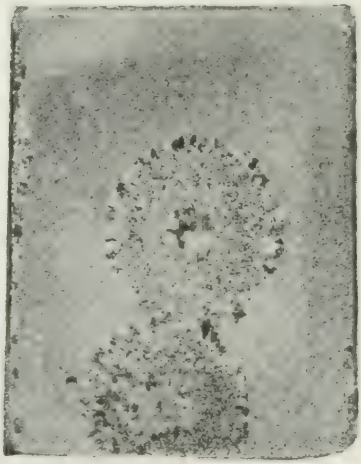


FIG. 75.—Effect on mild steel of local cold work with a steel ball, followed by annealing at 700° C.

DENDRITES AND CRYSTALS.

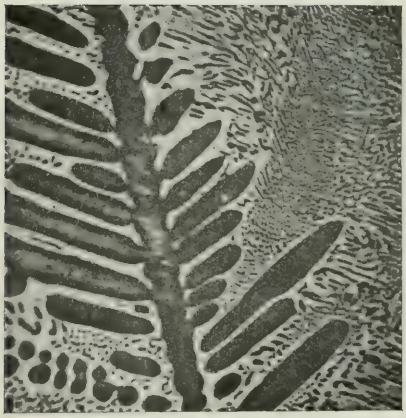


FIG. 76.—Silver-magnesium alloy, 15·4at.%Ag. Dendrites of Mg surrounded by a eutectic of Mg–Mg_3Ag. (ZEMZUZNYJ.)

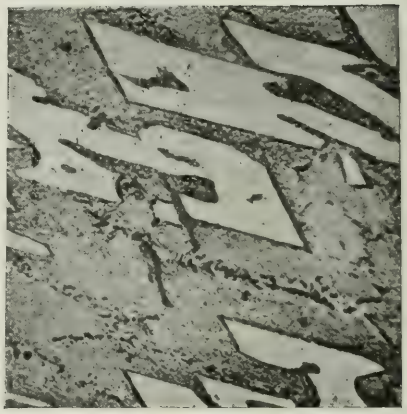


FIG. 77.—Silver-magnesium alloy, 18·9at.%Mg. Crystals of Mg_3Ag surrounded by Mg–Mg_3Ag eutectic. (ZEMZUZNYJ.)

DIFFERENT STRUCTURES EXHIBITED BY THE SAME EUTECTIC.

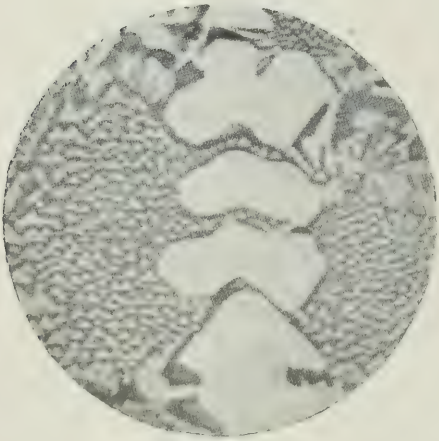


FIG. 78.—Alloy of antimony and Cu_2Sb. (DESCH.)

(× 200.)

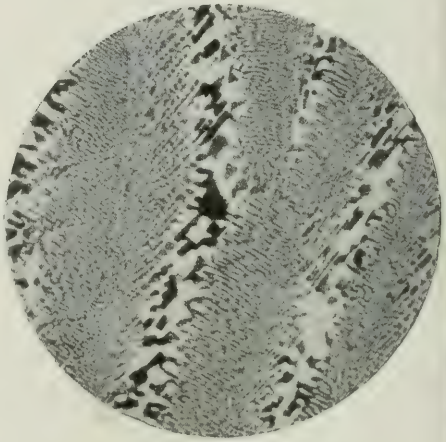


FIG. 79.—Eutectic alloy of antimony and Cu_2Sb. (DESCH.)

(× 200.)

EUTECTICS AND PRO-EUTECTIC CONSTITUENTS.

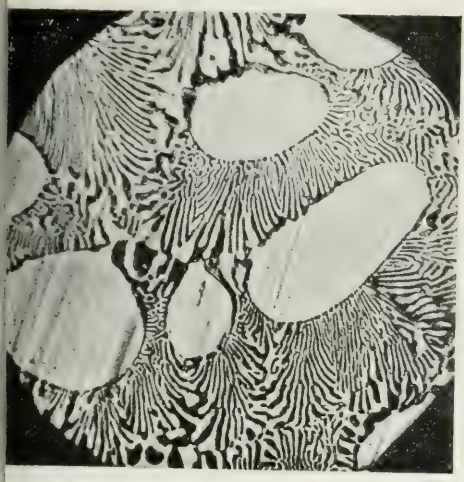


FIG. 80.—Phosphor-copper alloy, 9·06 % P.
Cu_3P surrounded by eutectic.
(HEYN & BAUER.)

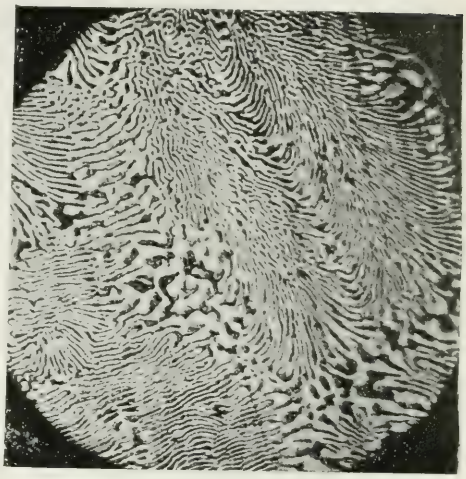


FIG. 81.—Phosphor-copper alloy, 8·2 % P.
Pure eutectic.
(HEYN & BAUER.)

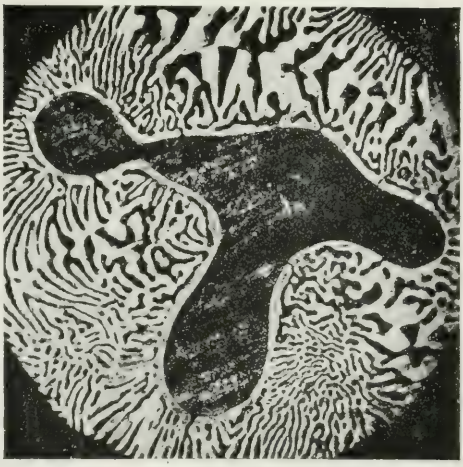


FIG. 82.—Phosphor-copper alloy, 7·25 % P.
Solid solution surrounded by eutectic.
(HEYN & BAUER.)

EUTECTICS AND PRO-EUTECTIC CONSTITUENTS (*cont.*).

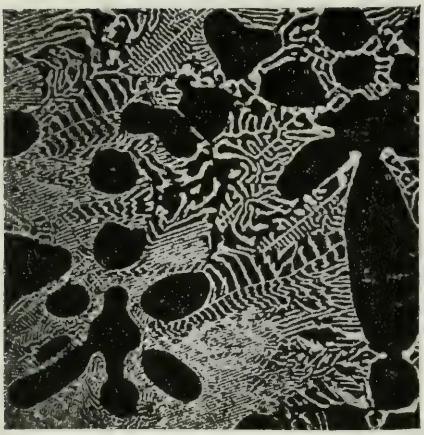


FIG. 83.—Magnesium-tin alloy, 8·0 % Sn. Dendrites of Mg surrounded by Mg–Mg_2Sn eutectic.

(KURNAKOW & STEPANOW.)

(× 100.)

FIG. 84.—Magnesium-tin alloy, 12 % Sn. Eutectic of Mg–Mg_2Sn.

(KURNAKOW & STEPANOW.)

(× 170.)

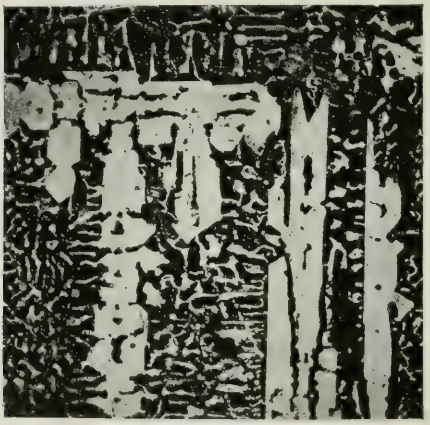


FIG. 85.—Magnesium-tin alloy, 13 % Sn. Crystals of Mg_2Sn surrounded by Mg_2–Mg_2Sn eutectic.

(KURNAKOW & STEPANOW.)

(× 70.)

EFFECT OF THE RATE OF COOLING ON THE SIZE OF THE STRUCTURE.

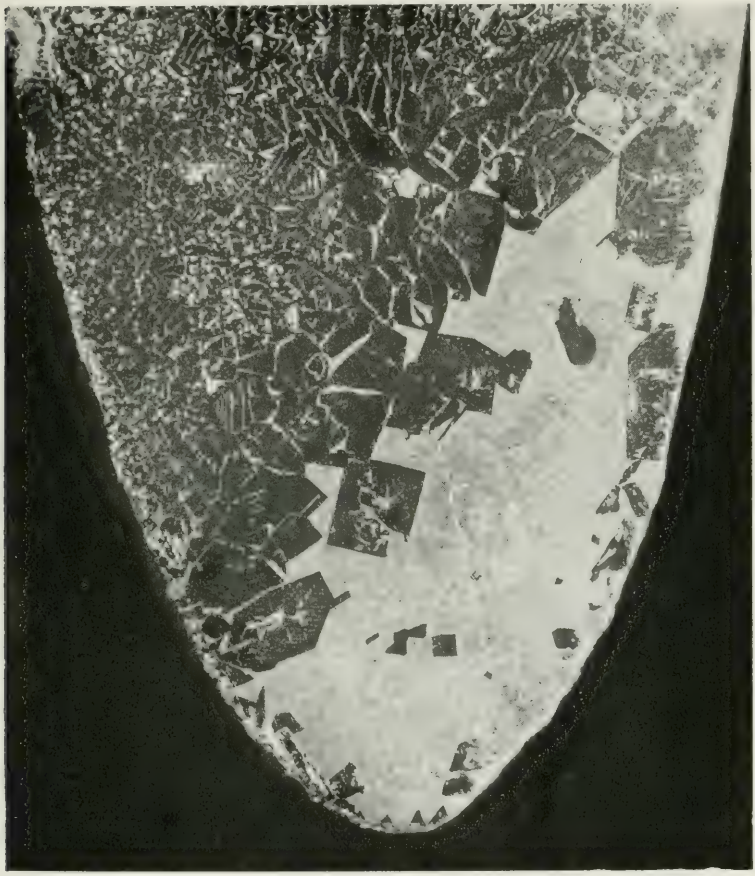


FIG. 86.—Antimony-lead alloy, 35 % Pb, very slowly cooled, unetched. (× 2.)

FIGS. 87-88.—**Alloy : 89·5 % Cu ; 10 % Al ; 0·4 % Mn.** (ROSENHAIN & LAGTSBERRY.) (× 100.)

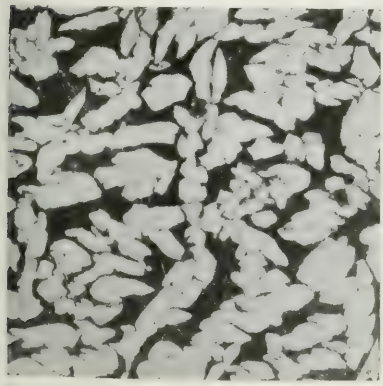


FIG. 87.—Sand cast.

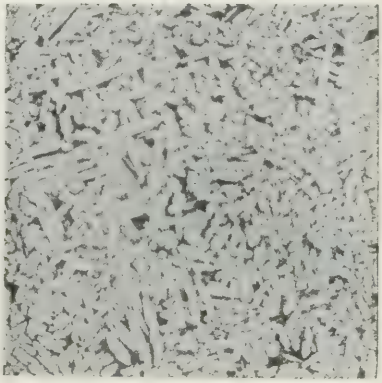


FIG. 88.—Chill cast.

NETWORK OR CELLULAR STRUCTURE AND WIDMANSTAETTEN STRUCTURE.

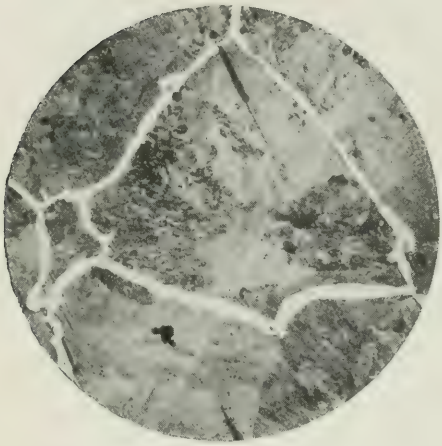


FIG. 90.—Hypoeutectoid steel. Network of ferrite in a background of pearlite. (N. T. BELAIEW.)
(× 30.)

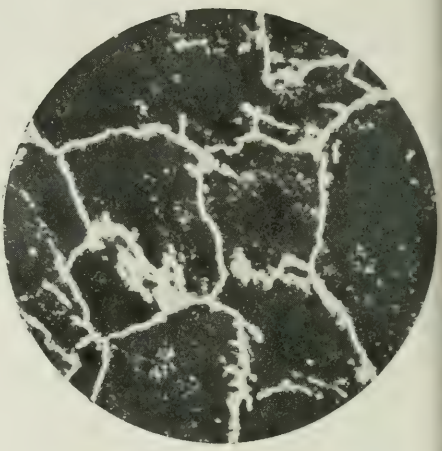
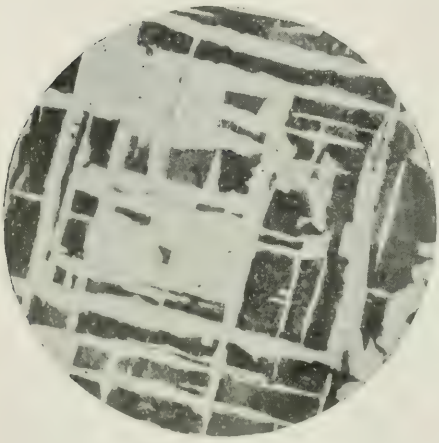
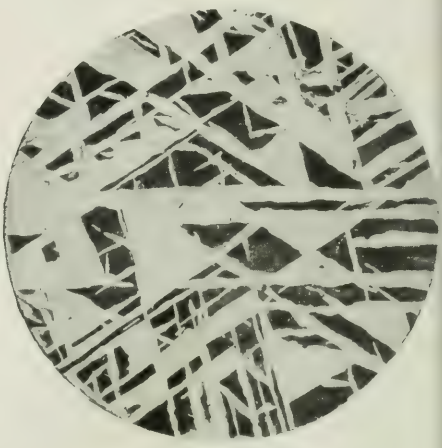


FIG. 91.—Hypereutectoid steel. Network of cementite in a background of pearlite.
(× 60.)

FIGS. 92–93.—Examples of Widmanstaetten Structure in Steels. (N. T. BELAIEW.)



C = 0·55 %. (× 35.)
FIG. 92.



C = 0·55 %. (× 30.)
FIG. 93.

2. During transformation each α grain forms a certain number of β grains; the α grains split up and there is an increase in the total number of grains. This is known as an indirect transformation. A transformation may be direct in one direction $\alpha \rightarrow \beta$ for example, and indirect in the opposite direction $\beta \rightarrow \alpha$.[1]

B. **Mixture of Two Phases**

As in the previous case, the structure will be examined at the time of formation and again after the various transformations have occurred, as these may modify the original structure when the mixture remains in a state of equilibrium.

A mixture of two phases may form, as it solidifies (as it passes from the liquid state), a very fine structure or, in the case of a transformation in the solid state of a single phase, a crystalline or granular structure, as already described. The form and distribution of the various constituents in the system will be different according to which of these two types the system belongs; both cases will now be considered.

The solidification of the single particles of the phases will be identical to the solidification of the individual particles of a single phase in the examples previously considered.

1. **Two Phases solidifying from the Liquid State.**—As already described, a mixture of two phases is obtained when the corresponding solidus is horizontal, in other words when solidification is completed either by the formation of a eutectic or by the solidification of the remaining liquid, due to a reaction (transition point) of the solid already formed with the liquid giving rise to another solid phase. In either case, solidification occurs during two periods.

(1) Progressive deposition of the first solid phase at varying temperatures forming the primary crystals—crystals of primary solidification.

(2) Completion of solidification at a constant temperature by the formation of a eutectic or by a reaction absorbing the remaining liquid. The filling or ground-mass between the crystals or grains of primary solidification is formed in the first case of eutectic and in the second case by another phase.

(*a*) *Primary solidification.*—During the first period, solidification proceeds as described with a single phase. Convex crystallites or dendrites separate from the liquid (Figs. 76, 77, Pl. VII.), and the temperature of complete solidification having been reached, the mass of the constituent varies proportionately with the total

[1] For further details refer to A. Portevin, "Contribution à l'étude de l'influence du recuit sur la structure des alliages" (*Revue de Met.*, vol. x. p. 677, 1913).

concentration of the alloy. The primary crystals or dendrites, as well as the surrounding liquid, are of definite composition.

(*b*) *Solidification of the eutectic.*—The saturated residual liquid, consisting of two phases, the one of identical composition to the solid phase already formed and the other of known composition, now solidifies at a constant temperature as an intimate mixture of these two phases (Figs. 80–85, Pls. IX. and IX. *cont.*, p. 72). The particles composing this conglomerate or eutectic are much smaller than the particles of the same phases formed during primary solidification under similar conditions, and can therefore only be resolved by the use of much higher magnifications than the magnification required to distinguish the particles of primary solidification. The constituents of a eutectic are often arranged as alternate lamellæ (example: pearlite in steels); in other instances they present a spotted, banded or grained appearance.

Under certain conditions it is possible for an alloy to exhibit two forms of eutectic structure, according to which of the two constituents of the eutectic is first deposited (Figs. 78, 79, Pl. VIII., p. 72) (Desch).

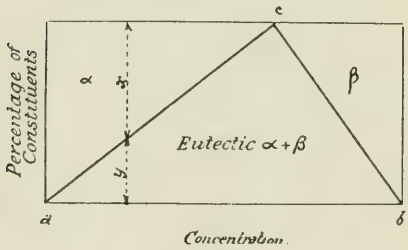


FIG. 89.

The grains or particles of primary solidification are not affected by the solidification of the eutectic, and they retain their original form, which they acquired before the solidification of the residual liquid. It is therefore usual for these grains of primary solidification to present a well-defined crystalline or dendritic structure.

In the above cases, if no modification or transformation occurs after solidification, the alloys will consist of primary crystals or crystal grains of α or β in a background or ground mass of $\alpha+\beta$ eutectic. The proportion of the primary crystals present will be directly proportional to the percentage composition of the alloy as indicated by Fig. 89.

The alloy contains *two constituents*: the one being the excess of α or β which solidifies from the liquid as crystals of primary solidification before the solidification of the eutectic; the other, the aggregate of fine particles of α and β forming the eutectic.

The relation

$$\frac{x}{y} = \frac{\text{primary } \alpha \text{ or } \beta \text{ in excess of eutectic}}{\text{eutectic}}$$

may be approximately estimated by measuring the areas of the surfaces of the two constituents of the alloy found in a section

viewed under the microscope; this measurement may be made by means of a planimeter. With practice it is possible to make a rough estimate of the composition by merely viewing the specimen under the microscope at a convenient magnification that shows a number of the individual grains in the field of view (estimation of the carbon content of hypoeutectoid steels).

The chemical composition of the constituents of the eutectic and of the eutectic itself may also be determined by extrapolation of the lines *ac* and *cb*.

By superimposing two metals in the liquid state and causing them to solidify before the mass becomes homogeneous, an ingot is obtained, a longitudinal section of which will show a continuous series of varying structures corresponding to all the alloys of these two metals. (Diffusion in the liquid state, Figs. 109, 110, Pl. XIV., p. 79.)

Size of the individual particles or crystals: liquation.—The size of the particles or grains of both the primary crystallisation and the eutectic increases as the time taken in passing from the liquid to the solid state increases; by very slow cooling one of the authors [1] has shown that certain alloys (lead-tin, copper-antimony, tin-bismuth, etc.) will form crystals which are clearly visible to the naked eye. Fig. 86, Pl. X. (p. 72), is an illustration of such an alloy (lead-antimony) in which the primary crystals of antimony are clearly visible and have accumulated owing to *liquation*. The liquation is a direct consequence of the progressive solidification in two stages. The primary crystals accumulate in the regions where the greatest cooling occurs (sides of the mould in the case of chill castings) or else, in cases where the density of the primary crystals differs from that of the liquid, tend to float to the top or sink to the bottom of the mass. This liquation causes the alloy to become heterogeneous, which fact can be verified by macrographical examination and by chemical analysis of metal taken from various parts of the casting.

Liquation or segregation is a very common occurrence with alloys and is an immediate consequence of the time taken by an alloy to solidify; in other words, the interval between the liquidus and the solidus. In the case of ingot metal casting, the portions solidifying last collect towards the centre of the upper portion of the ingot.

(*c*) *Transition point.*—Before the transition temperature is reached solidification proceeds by the separation of crystals or dendrites from the liquid. On reaching the transition temperature some or all of these particles or crystals react with the surrounding liquid to form another solid phase. The crystalline form of the

[1] Portevin, *Bull. Soc. Ing. civ.*, 66, 806, 1913.

primary crystals is thereby destroyed and the primary crystals may even entirely disappear. This reaction is, however, often incomplete owing to the *total envelopment* of the primary crystals of α by the new crystals of β, formed by the reaction with the liquid. This envelopment prevents further reaction taking place and permits the α phase to exist or persist in alloys which should not contain this phase ; an alloy of this type will consist of three constituents *not in equilibrium.* This case will be considered later (p. 83) as only alloys in a state of equilibrium are now being described.

2. **Mixture of Two Phases Forming in the Solid State.**—It has been shown that a solid α phase may react with a liquid phase to form, on solidification, a solid β phase along an oblique line of the diagram. In a similar manner it is possible for horizontal lines to be present, in the equilibrium diagram, below the solidus, indicating reactions at fixed temperatures, bringing about the formation of another phase or a eutectoid.

The two cases will be considered as regards their micrographic structure. If the physico-chemical laws governing these transformations are the same as those governing solidification, the genesis of the particles or grains is not identical, as, instead of crystallising from a liquid and consequently amorphous material, they separate in this case from a solid phase, which is a crystalline aggregate formed by the juxtaposition of the crystalline grains.

(1) In the case of a progressive separation of a β phase from an α phase, the particles of β might separate either between the α grains or inside them, forming two types of structure.

(*a*) The β phase separates between the α grains, forming an envelope for each grain, the structure being known as *cellular or network structure* (Figs. 90, 92, Pl. XI., p. 73).

(*b*) The β phase separates along the cleavage planes of the α grains, forming lamellæ in various directions. This structure is known as Widmanstaettens structure (Figs. 92, 93, Pl. XI., p. 73).

The above cases represent the two extremes possible, and as a general rule the structure obtained is an intermediate form comprising both these types.

Very slow cooling, giving a greater time for the separation of β, favours the production of the network structure. The rate of cooling has a similar effect on the grain size as it has during solidification (Figs. 87, 88, Pl. X., p. 72).

(2) In the case of the formation of a eutectoid, the original structure is entirely destroyed by the formation of an intimate mixture of the two constituents, the structures of which are extremely fine owing to their separation from a solid medium, the particles of which possess but little mobility. Other conditions being constant, the structure of a eutectoid increases in fineness as

the viscosity of the metal is greater and therefore as the temperature of formation is less. This eutectoid may exhibit a lamellar, granular, or network structure; several forms of structure may be found in the same alloy. One of the authors [1] has investigated this phenomena in the case of the γ eutectoid of the aluminium-bronze series.

Modifications in Structure of a Mixture of Two Phases in Physico-Chemical Equilibruim : Coalescence.—When a mixture of two phases is in physico-chemical equilibrium at a given temperature, that is to say when the chemical compositions and the respective properties of the constituents composing each of the phases are as defined by the equilibrium diagram, it is still possible for modifications in the structure to occur, such as change of shape or size of the particles; the particles assume the form of rounded grains, increase in size and consequently decrease in number since the total mass cannot change.

In this manner the eutectoid lamellar pearlite in steels changes to granular pearlite and finally separates into its two constituents, ferrite and cementite. In a similar manner the needles of cementite change into spheroidised cementite (Figs. 98, 99, Pl. XII., p. 78).

Analogous examples have been observed in the aluminium-bronze series (Figs. 94–97, Pl. XII., p. 78), the brasses and the copper-tin series.[2]

These phenomena of coalescence, which indicate the intervention of factors other than the temperature and pressure (the only physical changes taken into account in the construction of the equilibrium diagram), lead directly to the consideration of the *structural equilibrium* which all heterogeneous bodies tend to approach and which promotes the agglomeration of the particles or elements of each phase.

Coalescence is facilitated and is only to be observed in practice after raising the temperature; by this means it is possible to increase the size of the particles in a finely divided mixture of two phases and thereby permit the structure, previously irresolvable, to be resolved under the miscroscope.

Coalescence occurs in a similar manner during the formation of such structures, the slower the speed of formation, the larger the particles in most cases, hence the effect of the rate of solidification on the structure of alloys. Each particle of a phase being of a crystalline character, in other words, consisting of a single crystal or a mass of small crystals or crystallites constituting a single phase, all the phenomena described under a single phase will apply equally in this case.

During coalescence the growth of the particles occurs by the

[1] Portevin, *Inter Zeit. Metallogr.*, vol. iv. p. 257, 1913.
[2] Portevin and Bernard, *Revue de Met.*, vol. xii. p. 143, 1915.

progressive disappearance of the smaller particles at the expense of the larger particles; the heterogeneity of the alloy is increased corresponding to segregation in the solid state.

All the possible varieties of structure to be met with in binary alloys in a state of equilibrium have now been examined, and it has been shown that whereas the equilibrium diagram determines the chemical constitution, the texture and consequently the conditions of formation of an alloy, the phenomena of recrystallisation and coalescence, vary the structure according to the mechanical and thermal treatment to which it has been subjected; all these variations produce effects on the mechanical properties of the alloy. The modifications in structure of an alloy brought about by quenching and thereby retaining the alloy *not* in a state of equilibrium will now be considered.

Alloys not in Equilibrium

Whenever a transformation or reaction of any type shown on the equilibrium diagram does not occur, is only partially completed, or occurs at a different temperature to that shown on the diagram, the chemical constituents and the texture are no longer similar to those of an alloy in which all the transformations have occurred in a normal manner; the alloy is not in a state of equilibrium.

An alloy is said to be not in physico-chemical equilibrium when its chemical constitution does not correspond to that shown on the diagram, and it is not in structural equilibrium when the structure differs from that of an alloy in which all the transformations have occurred at the normal temperatures shown on the diagram.

From the above it will be observed that an alloy not in physico-chemical equilibrium cannot be in structural equilibrium, as structural equilibrium necessitates a state of physico-chemical equilibrium. The conditions of imperfect equilibrium may originate during solidification or during transformations taking place in the solid state.

The establishment of equilibrium is opposed by various internal causes; these have been classed under the general term of "interferences." These interferences lengthen the time taken to attain equilibrium and may even entirely prevent the return to equilibrium conditions.

As a general rule, it has been found that the effects of these various interferences decrease with a rise in temperature; it was due to this fact that the first equilibrium phenomena were discovered during an investigation on dissociation occurring at high temperatures.

These interferences operate in two ways:

1. By delaying the transformation.
2. By decreasing the speed of transformation.

COALESCENCE.

1° Copper-aluminium alloy : 10·78 % Al. (Carpenter & Edwards.)
(× 100.)

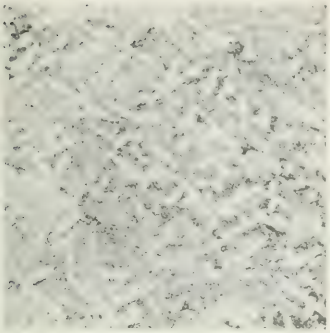


Fig. 94.—As rolled.

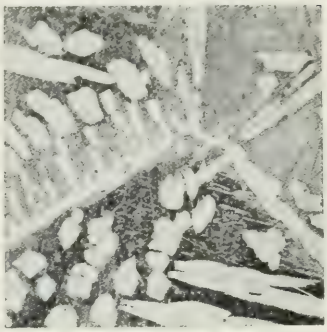


Fig. 95.—Annealed 1 hour at 900° C.

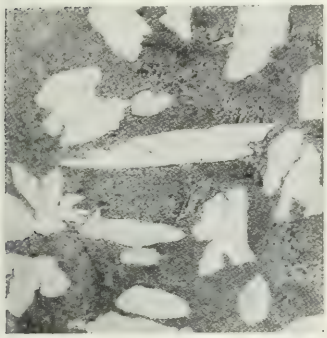


Fig. 96,—Annealed 7 hours at 900° C.

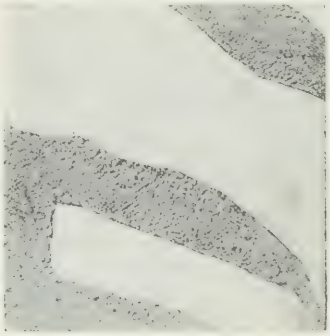


Fig. 97.—Annealed 30 hours at 900° C.

2° 1·43 % C. steel. Etchant : Bénédicks' reagent.
(× 1000.)

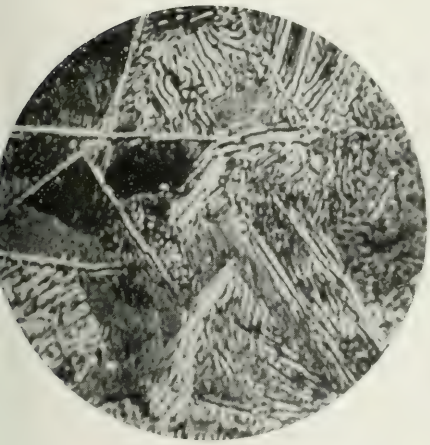


Fig. 98.—After forging.

Fig. 99.—After annealing at 850° C.

HETEROGENEOUS SOLID SOLUTIONS.

1° Alloy: 83 % Cu; 15 % Ni; 2 % Al.
Etchant: Acid ferric chloride.

FIG. 103.—Chill cast. Metal as cast.
(× 57.)

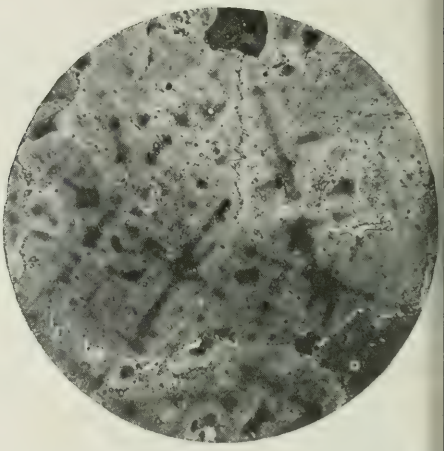


FIG. 104.—After annealing for 10 hours at 900
(× 57.)

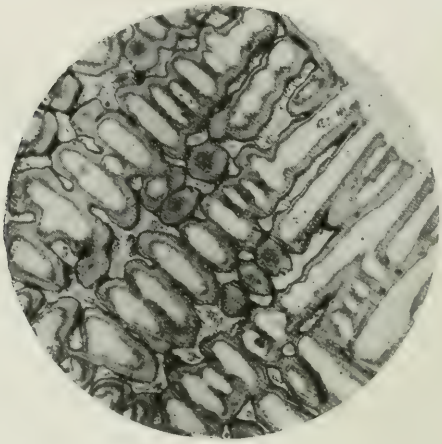


FIG. 105.—Chill cast. Metal as cast.
(× 200.)

HETEROGENEOUS SOLID SOLUTIONS.

2° Gold-copper alloy: 25 % Au.

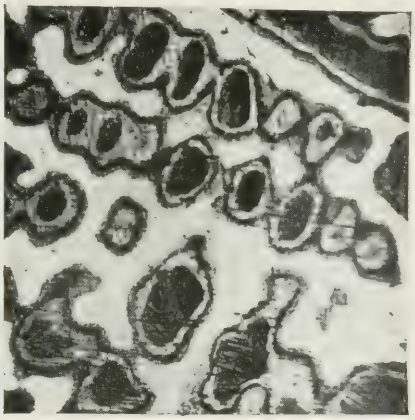


FIG. 106.—As cast. (KURNAKOW & STEPANOW.)
(× 20.)

3° Bronze: 5 % Sn. Etchant: Alkaline, H_2O_2.

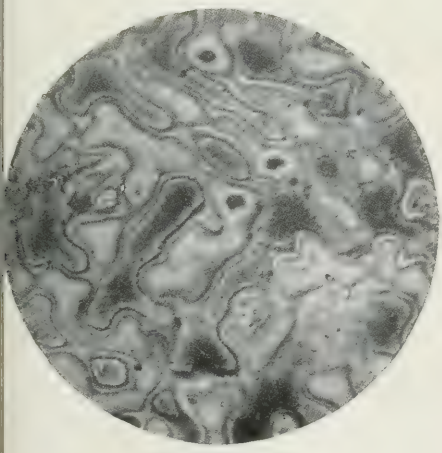


FIG. 107.—As cast.

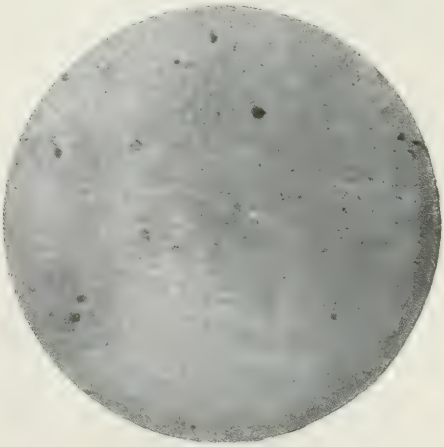
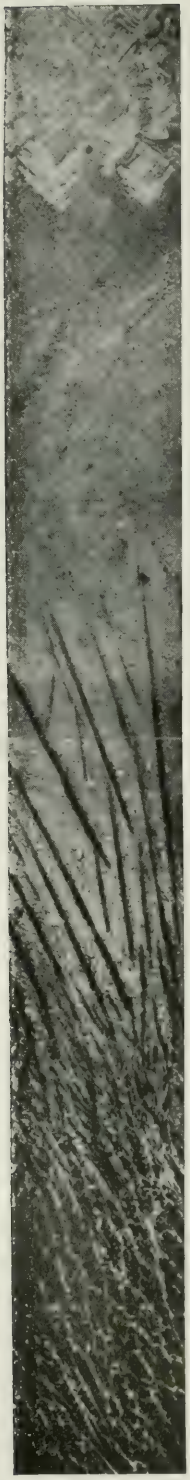


FIG. 108.—Annealed 3 hours at 800° C.

DIFFUSION IN THE LIQUID STATE.

Bi



Cd

FIG. 109.—Cadmium-bismuth.

Sn

Sb

FIG. 110.—Antimony-tin. (× 50.)

Delaying the transformation is merely a general description of the well-known phenomena of surfusion and supersaturation; the metal or alloy passes through the melting point and yet remains completely liquid: surfusion is said to have occurred; this surfusion may be avoided or prevented by a variety of means (shaking the mass of metal, introduction of crystal nuclei, etc.) or by a sufficient drop in temperature. In these circumstances there is a sudden liberation of heat causing the temperature to rise again. This phenomenon is known as *recalescence*, and finally the system attains physico-chemical equilibrium.

When the recalescence occurs at temperatures but little below the melting point, the temperature of liquid solid equilibrium is again reached and an arrest at this temperature may be observed

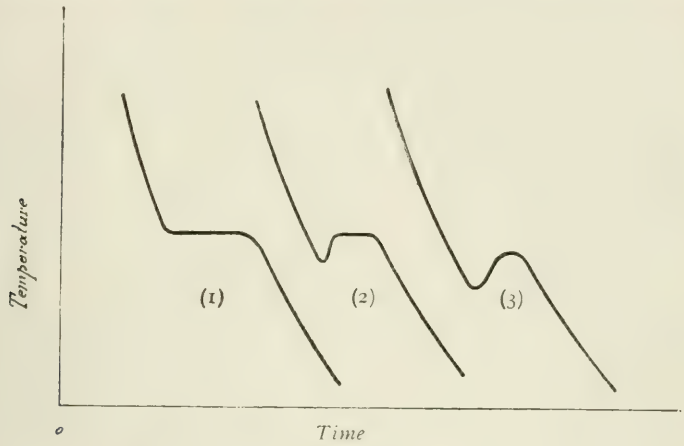


FIG. 100.

as shown in curve 2, Fig. 100; (this effect may nearly always be observed with antimony solidifying under ordinary conditions) but when the temperature at the commencement of recalescence is considerably lower than the melting point, the liberation of heat is no longer sufficient to raise the mass to the melting point and the type of curve illustrated as curve 3, Fig. 100, is obtained.

These phenomena may be observed equally well during the solidification of alloys, eutectics, etc., and in the course of transformations occurring in the solid state.

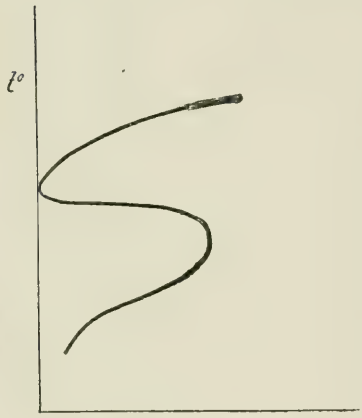
A sharp rise of temperature of this type always indicates that the system was not previously in equilibrium and that the speed of solidification or, more usually, reaction is very great at that moment. But the speed with which a reaction or transformation occurs at any temperature is, as with all chemical reactions, very much greater as:

1. The temperature is greater (interference effect lessened).

2. The temperature is more remote from the equilibrium transformation temperature.

Above the transformation temperature, on cooling, these two factors act in an inverse direction, such that on leaving and passing below the equilibrium transformation temperature the rate of transformation increases until it passes through a maximum, when it again decreases and finally becomes negligible at ordinary temperatures. The theoretical curve is of the form illustrated in Fig. 101 (Le Chatelier). For practical purposes transformation may be considered to cease at some definite temperature, varying with different alloys, and the alloy then remains in a state of imperfect equilibrium.

Above this temperature, the speed of transformation is appreciable and a system in imperfect equilibrium tends to attain equilibrium conditions; this phenomenon is known as tempering (steels) or annealing. In practice, it is possible to find a definite temperature at which the tempering or annealing effect commences, but the temperature will vary with the sensitivity of measurement and the particular property investigated.



Rate of Transformation

FIG. 101.

Moreover, the temperatures corresponding to the maximum rate of transformation and minimum annealing temperature are both dependent on many factors.

It is now obvious that if an alloy with a known transformation point is cooled sufficiently rapidly, this transformation may be partially or entirely suppressed, owing to the short space of time that elapses before a temperature is reached at which the transformation can no longer occur or cannot be complete; but under these conditions the transformation may also occur over a range of temperature below the true transformation temperature, and this interval of temperature will be indicated by the liberation of a variable quantity of heat. Because of these phenomena it is stated that *the transition temperature is lowered by an increase in the rate of cooling.*

It is only recently that the relation between the transition point of steels on cooling and the rate of cooling has been investigated.[1]

The lowering of the transition point does not only depend on

[1] Portevin and Garvin, *C. R.*, vol. clxiv. p. 885, 1917. Chevenard, *C. R.*, vol. clxv. p. 59, 1917.

the rate of cooling or more correctly the law of cooling, but also on the presence of various foreign bodies, temperature, and the time of heating.[1]

Inversely, on heating an absorption of heat will occur at temperatures higher than the equilibrium transformation temperature, hence the distinct transformation temperature on heating. The interval between the transformation temperatures on heating and cooling is known as the *thermal hysteresis*. The hysteresis is dependent on the following factors: the chemical composition of the alloy, the temperature, the laws of heating and cooling, the maximum temperature reached during the heating operation.

When a transformation, accompanied by change in volume, occurs at comparatively low temperatures, the metal being but slightly malleable at these temperatures, the change in volume increases the internal stresses within the metal and these tend to oppose the transformation (in accordance with Le Chatelier's principle) and also cause internal strains which considerably modify the mechanical properties of the alloy.

Effect on the Structure—Transition Constituents—Constituents in Imperfect Equilibrium.—By rapid cooling it is possible to obtain at ordinary temperatures:—

1. Alloys in which the transformation has been partially or entirely suppressed.

2. Alloys in which the transformation has occurred through a range of temperature below the equilibrium temperature.

It is therefore possible to examine constituents which exist at high temperatures and which have been preserved at ordinary temperatures but not in a state of equilibrium (example: austenite in steels).

Further, it has been shown that the more rapid the transformation, the finer is the structure; the particles may even be so fine that they cannot be resolved by the highest magnifications at present available, hence the hypothesis of colloidal solid solutions (troostite in steels); again, the internal stresses produced by transformations at comparatively low temperatures, accompanied by changes of volume, give rise to a macled structure due to deformation (martensite in steel), and finally the separation of the constituents will probably be intra-granular; the last two factors bring into evidence the cleavage planes of the solid solution which were in existence before the transformation occurred.

The effect of the above phenomena is to enable an alloy to

[1] The effect of the temperature and time of heating clearly indicates the part played by the crystalline nuclei in the retardation of transformation (see Osmond, *Revue de Met.*, vol. i. p. 348, 1904), also observed by Wyrouboff in the case of polymorphic transformation in certain salts (see Portevin, *Revue de Met.*, vol. x. p. 720, 1913).

present several different structures, each possessing different properties and which all differ from those of the original alloy in a state of equilibrium. These constituents will be termed *transitional constituents.*

In every case there is a definite correlation between the structure and the temperature of the transition point at the time of cooling which has produced the structure.

Reheating restores, when necessary, the physico-chemical equilibrium, destroys the effects of the internal strain, and, by the coalescence of the fine or ultra-microscopic particles, restores the structural equilibrium.

Non-homogeneity of Solid Solutions.—The solidification of a solid solution may be chosen as a specific instance of an incomplete reaction. It has been supposed, in describing the progress of this type of solidification (p. 30, *cont.*), that the particles or crystals of the solid phase assume the equilibrium composition at each temperature, as indicated by the solidus of the diagram, and it was stated that this necessitated diffusion in the solid state within the crystals; the rate of such diffusion is so slow that, in the solidification of commercial alloys, homogeneity of the solid phase is rarely attained except, perhaps, in cases where the liquidus and solidus are separated by only a few degrees. Consider as an example the case illustrated by Fig. 102. Equilibrium is attained at each temperature only between the outer layer of the particles of the solid phase and the liquid phase; these particles, therefore, have a zoned structure and are formed of layers successively richer in B towards the outside; also at any given temperature the mean composition of the solid phase will be found richer in A than is required by the equilibrium diagram. The temperature t' being reached, which is the temperature of complete solidification of the homogeneous alloy, there still remains some liquid, as the solid phase has not taken up its full quantity of B; solidification is complete at a temperature t'_1, less than t; with progressively increasing rates of cooling, the temperature of complete solidification is still further lowered until it finally coincides with the melting point of B at a temperature t'_3.

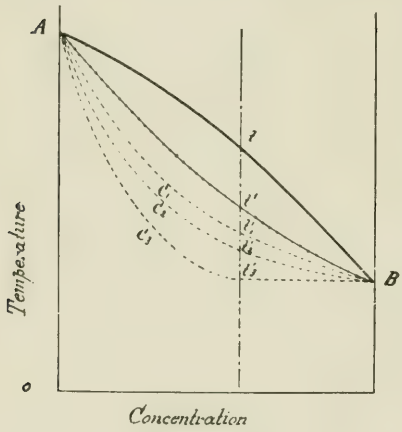


FIG. 102.

The curve showing the completion of solidification at a definite rate of cooling is given by AC_1B; other rates of cooling are

represented by the curves AC_2B, AC_3B; in the last case the horizontal portion of the curve corresponds to the solidification of pure B.

It is possible to have not only heterogeneity of the solid solution (Figs. 103, 105, Pl. XIII, Figs 106, 107, Pl. XIII. *cont.*, *see* p. 78), but also the presence of other constituents such as eutectics not in a state of equilibrium.

Annealing, by allowing diffusion to take place, permits the system to attain equilibrium conditions and the constituents of imperfect equilibrium disappear.

Examples: α bronzes (Figs. 107, 108, Pl. XIII. *cont.*), copper-nickel alloys (Figs. 103, 104, Pl. XIII., p. 78).

Incomplete Reactions due to Envelopment.—If, during the solidification of an alloy, the crystals A react with the surrounding liquid L to form a compound C, the compound may completely enclose the crystals A and separate it from the liquid, thus stopping the reaction; the reaction may occur by diffusion, the compound C being superficially substituted on A, or in the case of the reaction occurring at the centres of crystallisation of C, these centres attach themselves to the surface of A, ; their number, especially if the reaction is much delayed, may be very great per unit of surface. In both cases, the reaction is incomplete. Crystals are obtained which may possess a regular external shape, but which consist of A in the centre and C on the surface. This phenomenon has been identified in the formation by reaction (transition temperature) of numerous definite compounds. Examples: $AuPb_2$, $AuSn_4$, Sb_2Cr, Ni_4Sb_3, Cu_2Cd, NiSn, SnMn (Figs. 113, 114, Pl. XV.); Fe_3Sb_2 (Figs. 111, 112, Pl. XV.). One of the authors [1] has even found, in the case of the nickel-bismuth series, two incomplete reactions occurring in succession, thereby producing four constituents, Ni, NiBi, $NiBi_3$, Bi.

When the diagram is constructed from thermal analysis observations, indications of incomplete reactions are given by discordances in the slope of the curves at temperatures corresponding to the horizontal lines of the diagram.

These binary alloys presenting more than two constituents at atmospheric temperature are not in equilibrium, and remain in this state. It is possible by prolonged annealing, at temperatures approximate to the reaction temperatures, to render the reaction more complete, but any such change will take place very slowly.

Labile and Metastable Equilibrium

It is possible in the case of alloys not in equilibrium, owing to the reactions or transformations having been entirely suppressed, to establish a definite state of equilibrium according to another

[1] Portevin, *Revue de Mét.*, vol. v. p. 110, 1908.

set of lines, or perhaps the same set of lines of the diagram further extended; this state of equilibrium, less stable than that previously indicated, has received the name of metastable state or labile equilibrium. Example: Let M be a transition point (Fig. 117) corresponding to the successive deposition of two compounds C_1 and C_2 on passing from the liquid state; an alloy of composition corresponding to the vertical PN ought, on cooling, to deposit C_2 on passing through P; if, on the other hand, it remains surfused as regards C_2 it will remain in the liquid state below (L_2); but, in this liquid, it is possible to establish, with C_1, a state of equilibrium by the deposition of C_1 on passing through N′, which is the point of intersection of PN with (L'_1), extension of (L_1); there then exists in the shaded region a system (liquid+C_1) in equilibrium in the presence of C_1, but not in the presence of C_2 which is the stable form; such an equilibrium is termed labile equilibrium.

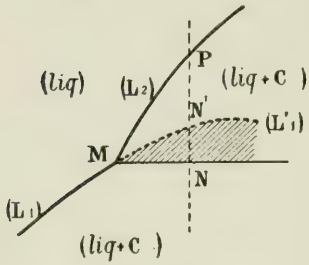


FIG. 117.

Below the temperature MN, C_1 is the stable form and C_2 the labile form. It is thus possible, owing to surfusion or suppression of transformations, to observe the extension of the lines of the stable equilibrium diagrams beyond their points of mutual intersection; the line of labile equilibrium being below that of stable equilibrium. Therefore, in this case, the diagram is completed by the lines of labile equilibrium, which may be either extensions of the lines of stable equilibrium, or completely below these lines.

The alloys of the cadmium-antimony series may be cited as an example (two compounds CdSb and Cd_2Sb_3 unequally stable according to the position on the diagram). Zinc-antimony series (two compounds ZnSb and Zn_3Sb_2 unequally stable, Figs. 115, 116, Pl. XVI.; iron-carbon series (stable form of carbon, graphite; labile form, Fe_3C).

An alloy in labile equilibrium always tends to pass into the condition of stable equilibrium. This change may occur spontaneously at some definite temperature, and be accompanied by a sudden liberation of heat, or if the interferences exert a great influence the change may occur slowly and progressively; as the effect of the interferences decreases with rise of temperature, the change takes place more easily at high temperatures. It is possible that the interferences may be such that the change can only occur at high temperatures and at certain concentrations in the series of alloys.

The labile and stable constituents may be present in an alloy simultaneously, this condition being frequently present with cast irons (Figs. 117, 118, Pl. XVI.).

As a general rule, any irreversible liberation of heat on cooling

BINARY ALLOYS WITH 3 CONSTITUENTS NOT IN EQUILIBRIUM, ILLUSTRATING INCOMPLETE REACTIONS DUE TO THE ENVELOPMENT OF ONE CONSTITUENT.

Antimony-iron alloy : 20 % Fe.
(× 200.)

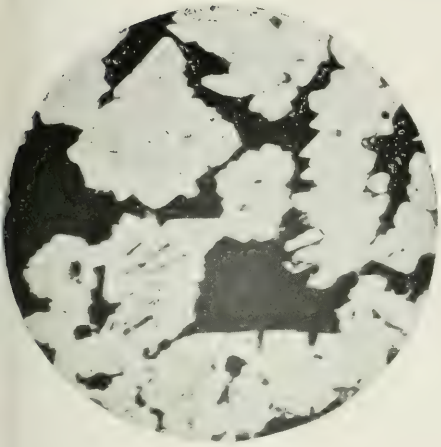


FIG. 111.—Etched for 5 secs. in copper-potassium chloride.

FIG. 112.—Etched for 5 secs. in copper-potassium chloride, followed by 10 secs. etching in acid ferric chloride.

Manganese-tin alloy : 32 % Mn.
(× 100.)

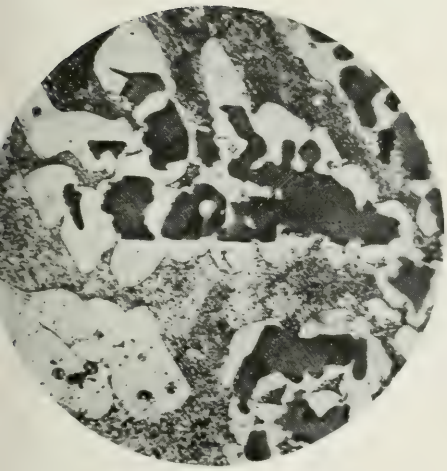


FIG. 113.—Etchant : Picric acid.

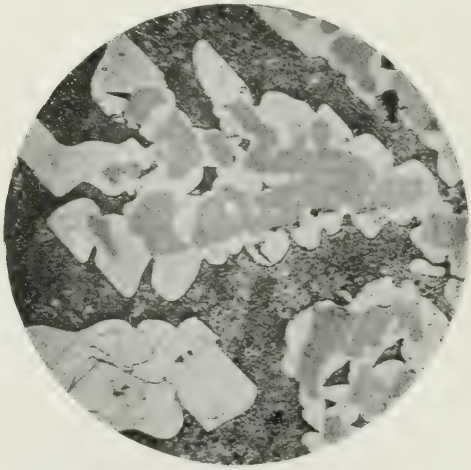


FIG. 114.—As polished.

STABLE AND LABILE EQUILIBRIUM.

Antimony-zinc alloy : 78·5 % Sb. (ZEMZUZNYJ.)

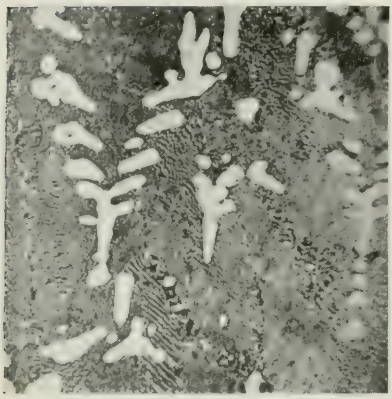


FIG. 115.—White unstable crystals of antimony in an unstable eutectic mixture of antimony and Zn_3Sb_2. Etchant : Nitric acid.

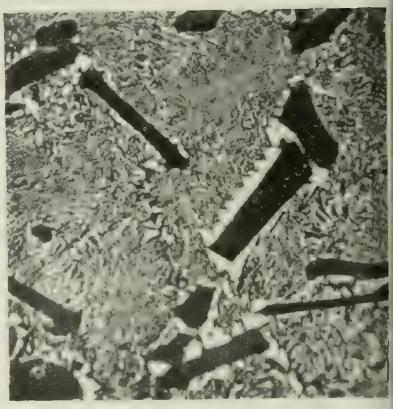


FIG. 116.—Dark primary crystals of sta ZnSb in a stable eutectic of Sb + Zn Etchant : Nitric acid.

Grey cast iron (C = 2·88 ; graphite = 2·48 ; Mn = 0·42 ; Si = 2·16).
(× 250.)

Stable graphite and pearlite.—Labile cementite and pearlite.
The two micrographs show the same field.

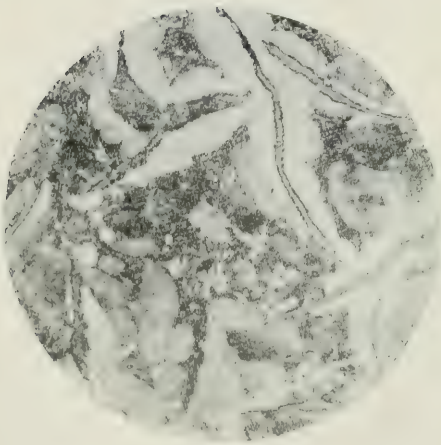


FIG. 117.—Ferrite and cementite, light.
Graphite and pearlite, dark.
Etchant : Picric acid.

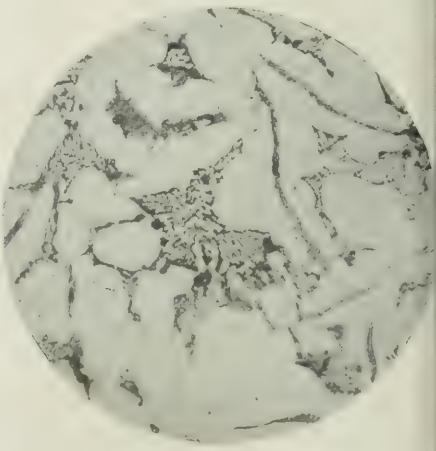


FIG. 118.—Ferrite and pearlite, light.
Graphite and cementite, dark.
Etchant : Sodium picrate.

characterises the previous existence of a state of labile equilibrium; similarly, any liberation of heat on heating indicates the previous existence of the system in imperfect equilibrium.

Verification of the Diagram by the Examination of the Microscopic Structure of the Alloys

The relation between the microscopic structure and the equilibrium diagram has been shown, in the case of alloys in a state of equilibrium, by the examination of various alloys at ordinary temperatures, any irregularities of the structure indicating imperfect equilibrium: verification of the fact that the alloy is not in equilibrium may be obtained by the examination of the variations of the microstructure which are brought about by varying periods of annealing, followed by slow cooling; the relation between the structure, at atmospheric temperature and variable concentrations, and the equilibrium diagram is thus complete.

Inversely, with any given alloy it is possible to obtain certain additional evidence with regard to the equilibrium diagram at varying temperatures, by the examination of quenched specimens.

1. If any alloy is not in a state of equilibrium due to the suppression or retardation of a transformation normally occurring at a temperature T, any heating or annealing at a temperature below T will tend to modify the structure and restore the alloy to a state of equilibrium; if this change can be clearly seen under the microscope, it will be possible to verify the stability of this structure until the temperature T is reached, and also to find the minimum temperature at which the transformation commences.

2. Inversely, if an alloy, in a state of equilibrium, is quenched at gradually increasing temperatures, it will be possible, at temperatures above the transformation temperature T, to obtain alloys which are not in equilibrium, this condition being proved by the change in the structure, and also to find the upper limit of the transformation T.

It was by means of this method—quenching specimens at gradually increasing temperatures—that Heycock and Neville traced the solidus for the copper-tin system, Gutowski the solidus of the iron-carbon series, Wark, Goerens, Meyer and Saldaou the transformation curves of the iron-carbon diagram. As a general rule it is essential to verify the relative stability of any structure by prolonged annealing; in fact, annealing, by the operation of the phenomena of diffusion, coalescence and liquation in the solid state:

1. Brings about the chemical homogeneity of solid solutions.
2. Increases the chemical heterogeneity of more than one phase.

By this double action the operation of annealing is of great assistance in verifying whether more than one phase is actually present.

CHAPTER III

THE MECHANICAL PROPERTIES AND TREATMENT OF METALLURGICAL PRODUCTS

THE object of this chapter is not to give a complete description of the various mechanical properties and treatments to which metallic products may be subjected, but merely to give a general outline of the various mechanical tests and treatments in common use and to show their relation with the equilibrium diagram and consequently the structure of the material.[1]

MECHANICAL TESTS

Introduction.—In order to ensure that the quality of any metal or alloy is up to standard it is usual to submit samples to various mechanical tests ; these tests enable the value of the various strength coefficients of the material to be determined and it may then be compared with other material of a similar nature, or employed for a similar purpose.

Mechanical tests may be divided into two main categories :—

Acceptance tests which various classes of material have to undergo to ensure that they satisfy the specification or are satisfactory for the purpose required.

Laboratory tests carried out on various material before it leaves the works and is put into commercial use and also on material which has failed during use—mechanical failures.

Acceptance tests may be subdivided into two main classes :

Mechanical tests, the results of which are stated in figures (tons, sq. ins., ft.-lbs., etc.).

Works tests to ensure that the material is satisfactory for certain uses ; examples : soldering and brazing tests, bending tests, drift tests, machining tests, etc., etc., closely approaching the actual nature of the treatment that the material has to undergo during the course of manufacture.

It must be observed that the results obtained from such tests are largely dependent on the method of carrying out the test, and

[1] Full details may be found in Guillet : *Trempe, Recuit, Revenu,* Dunod and Pinat, Paris, publishers.

are therefore dependent on the workman. In spite of this, the introduction of such tests into many works has greatly lessened the difficulties encountered.

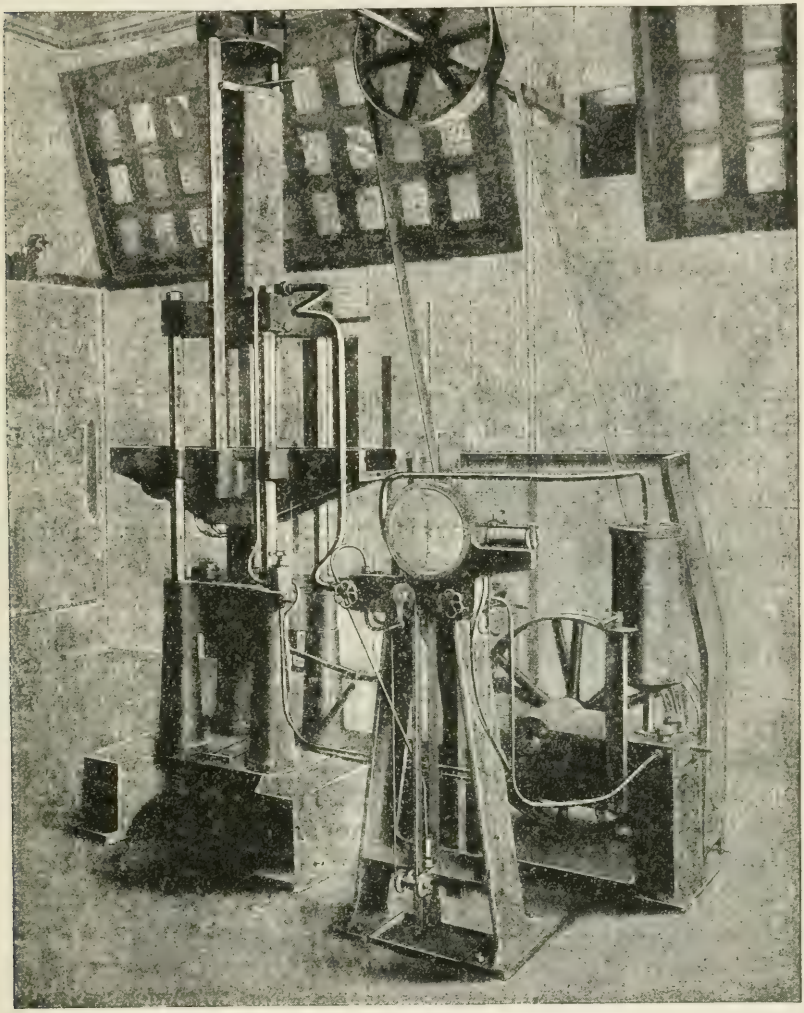


FIG. 118.—Amsler-Laffon tensile testing machine.

The mechanical tests, the results of which are stated in figures, are :—

Tensile tests ;
Compression tests ;
Bending tests ;
Impact tests on plain or notched specimens ;
Hardness tests ;
Punching, bending, drifting, and torsion tests.

Tensile Tests

In this test the specimen is subjected to a direct pull which gradually increases until the specimen breaks.

Coefficients defined by the Tensile Test.—This test permits the following important coefficients to be determined:

1. *The ultimate strength in tons per square inch,* denoted by the letter R. This is the maximum load that the metal is able to support per square inch of the initial cross-section before breaking. Let S be the initial cross-section of the specimen in square inches, and R_T the total load in tons supported by the specimen before fracture, then the ultimate strength of the material is given by the expression

$$R = \frac{R_T}{S}$$

2. *The elastic limit in tons per square inch,* denoted by the letter E. This is the maximum load that the metal is able to support per square inch of cross-section without undergoing any permanent deformation.[1]

By permanent deformation is meant any deformation which exists after the removal of the strain.

The elastic limit must be distinguished from the yield point.

If a tensile test be carried out on any material, the strain (extension) at each stress (load) being measured, and such strains are plotted against the corresponding stresses, a diagram is obtained which is known as the *stress-strain diagram.* For most metals the stress-strain diagram will be a straight line until a certain point is reached, called the *elastic limit*—limit of proportionality.[1] After which the strain increases more rapidly than the stress, until at a certain point there is a sudden large increase in strain for a comparatively small increase in stress. This point is known as the *yield point.*

Let S equal the initial cross-section of the specimen in square inches, and E_T be the load at which the specimen commences to be permanently deformed, then:

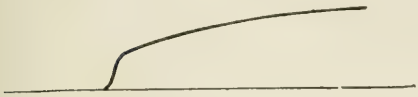
$$E = \frac{E_T}{S}$$

3. *Percentage elongation after fracture* (A per cent.).—This measurement is obtained from specimens of standard gauge lengths, the gauge length varying with the diameter of the specimen.

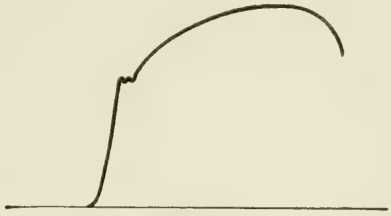
[1] From this definition it will be observed that the value of the elastic limit will depend on the sensitivity of the instruments employed.

Let l be the original gauge length of the specimen, L the length of the same section after fracture, then :

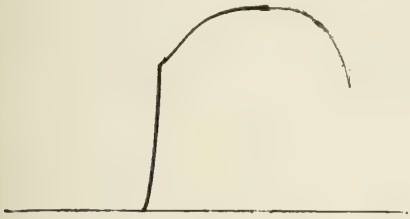
$$\text{A per cent.} = \frac{L - l}{l} \times 100$$



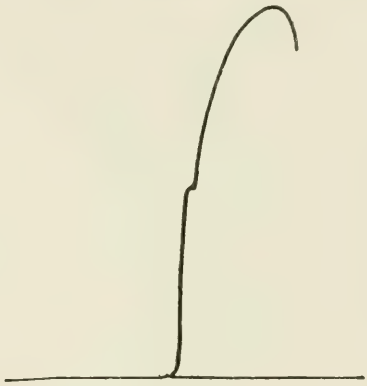
Curve 1.



Curve 2.



Curve 3.



Curve 4.

Curve 5.

(All the curves were obtained on the same machine.)

Curve 1.—Brass with very low elastic limit.
Curve 2.—Mild steel showing yield point.
Curve 3.—Very mild steel.
Curve 4.—Medium carbon steel with average elastic limit.
Curve 5.—Medium carbon steel with high elastic limit.

FIGS. 119–123.—Stress-strain diagrams.

(Strain as abscissæ, stresses as ordinates.)

4. *Percentage reduction in area of cross-section,* denoted by Σ.

Let S be the initial cross-section of the specimen, s the smallest area of cross-section after fracture (this is not necessarily the area of the fracture), then :

$$\Sigma = \frac{S - s}{S} \times 100$$

Importance of the Different Coefficients.—The following remarks will illustrate the importance of the various coefficients.

The ultimate strength R gives the maximum load that the

material is able to support and allows a factor of safety to be determined.

The elastic limit E gives the maximum load that the material will support before being permanently deformed or having a "permanent set."

The percentage elongation, A per cent., and the percentage reduction in area Σ give an indication of the ductility possessed by the metal.

Determination of the Various Coefficients.—The determination of these various coefficients is carried out by means of mechanical testing machines, in which the test-piece is held in clamps between two jaws or it may be threaded into clamps at each end.

In modern machines the clamps are suspended from double universal joints to ensure that the specimen is stressed only along one axis. The load, which is increased slowly and regularly, is applied either by hydraulic pressure or by some mechanical means which serves to move one jaw or clamp (generally the lower jaw) in relation to the other. The load is measured by attaching the stationary jaw to the short arm of a balance provided with a "jockey weight" on the other side of the knife-edges. The load is balanced by moving the jockey weight along the beam, this condition being indicated by a small pointer or other device moving over a scale. In the case of some hydraulic machines a pressure gauge is the means of measuring the load, the diameter of the cylinder being known the load is easily calculated; but this method is not reliable as it is dependent on the accuracy of the gauge.[1]

Frequently the load is recorded on a chart by means of an "autographic recorder," consisting of a revolving drum intergeared with the machine in such a manner that a stress-strain diagram is automatically plotted on the sheet of ruled paper placed round the drum.

Briefly, a tensile testing machine consists of the following parts:

1. The apparatus to apply the load or stress.

2. The apparatus to hold the specimen and connect it to the above.

3. The apparatus to record the load or stress.

A brief description of the methods employed to obtain the values of the various coefficients may now be given:

1. The ultimate strength is derived from the maximum registered on the machine; when an autographic record is taken, this load is the maximum value shown on the curve.

[1] The description of various tensile testing machines does not come within the scope of the present work. The most modern forms are those of the Amsler-Laffon type, and readers are referred for further particulars to Martin's text-book of the subject, translated by Breuil, Gauthier-Villars, publishers, and also to various articles by Breuil in the *Revue de Mecanique*. Translator's note: Also Ewing's "Strength of Materials" and Unwin's "Testing of Materials of Construction."

2. The yield point is more difficult to obtain. With testing machines of the Thomasset or Maillard type it is indicated by an arrest in the rise of the mercury column, but this type of machine is now very little used. With ordinary straight-beam or multiple-lever type machines it is indicated by a drop of the beam, as the extension takes place more rapidly than the increase of load. It is shown on the autographic record (stress-strain diagram) by an arrest, alteration of direction in the curve, or the point where the curves deviate from a straight line.

The Elastic Limit is far more difficult to determine and can only be found by means of a very accurate measuring apparatus known as an Extensometer. There are many forms of this apparatus, descriptions of which may be found in any of the standard works on the testing of metals. By means of the extensometer measurements of the extension are taken for small increments in the load and the results obtained are plotted. The limit of proportionality or the true elastic limit can then be determined from the curve by noting the point at which the curve deviates from the straight line. There appears little doubt that the value of the elastic limit, with the load applied in any one direction, is not the same throughout the whole mass of the sample, but that there is a minimum value for certain crystals and a maximum value at which all crystals are deformed, the value being dependent on the orientation of the respective crystals.[1]

This is very clearly illustrated by the method introduced by Frémont: a perfectly polished conical test-piece (Fig. 124) is sub-

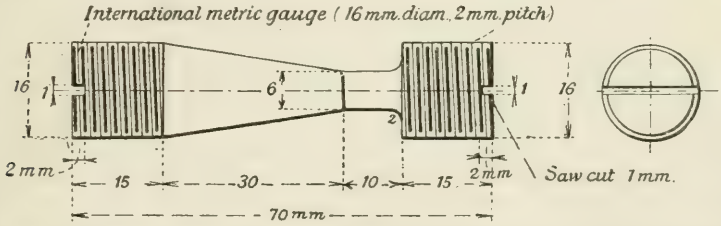


FIG. 124.—Frémont's tensile test-piece for the determination of the elastic limit.

jected to a load greater than the ultimate strength of its smallest section.

The polished surface of the specimen is destroyed over the whole of that portion of the specimen subjected to a load greater than the elastic limit. By microscopical examination, the point along the specimen, where the polished surface ceases is easily seen (Pl. XVII. Figs. 125, 126, p. 114); and dividing the total load by the

[1] See A. Portevin, "Sur la limite élastique des alliages," *C. R.*, 156, 1237, 1913. "Sur les déformations microscopiques des alliages." Meeting on May 31, 1913, of the International. Assoc. for the Testing of Materials.

area of cross-section at this point in square inches gives the elastic limit in tons per square inch.

Experimentally, it is practically impossible to determine the exact limits of the polished and distorted sections except in the case of alloys having a distinct yield point, in which case this point is also clearly seen on the stress-strain diagram. In practice, there is found an area which has been very slightly de-polished and an area entirely de-polished, corresponding to the minimum and maximum values of the elastic limit,[1] both of which determinations afford valuable information as to the properties of the metal under test.

3. The percentage elongation may be read from the stress-strain diagram, but is more easily obtained by direct measurement of the fractured specimen when the two portions are fitted together as accurately as possible. It is usual, before testing, to mark off the *gauge length* by means of two light centre-punch marks a given distance apart (2 ins., 4 ins., 100 cms.), the distance depending on the diameter of the test-piece. Measurement after fracture gives the increase due to the elongation of the specimen and the percentage elongation is easily calculated. If a stress-strain diagram is to be taken, two clamps are fixed to the test-piece and register in the centre-punch marks. Wires are attached to these clamps and suitable gearing, etc., enables the elongation to be recorded on a revolving drum.

4. The percentage reduction in area of cross-section is determined by the direct measurement of the initial cross-section of the test-piece and the smallest cross-section after fracture.

Precautions to be taken in carrying out tensile tests.—Numerous precautions are necessary if the results of tensile tests are to be comparable with each other :—

1. It is essential that the test-pieces shall be homologous ; the relation between the gauge-length (used in the measurement of the percentage elongation) and the cross-section is represented by the equation

$$L = K\sqrt{S}$$

In France the proportion is usually

$$L = \sqrt{66{\cdot}678}$$

The most general form of test-piece is of circular section, gauge length 100 mm., diameter 13·8 mm. An illustration of this type of test-piece is shown (Fig. 127). When testing sheet metal, the thickness of which is a limiting dimension, the width of the test-piece is varied to give the constant ratio of length to cross-section.

2. Influence of time in the process of testing. If the test is

[1] See A. Portevin, "Sur la limite elastique des alliages," *C. R.*, 156, 1237, 1913. "Sur les déformations microscopiques des alliages." *Proceedings* May 31, 1913, International Assoc. for the Testing of Materials.

carried out more rapidly the ultimate stress and the elastic limit are increased whilst the percentage elongation is decreased.

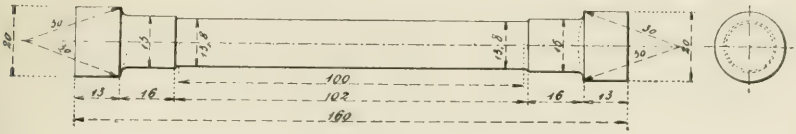
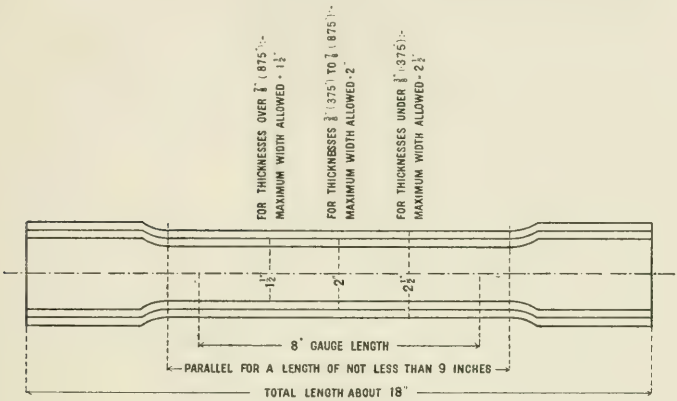
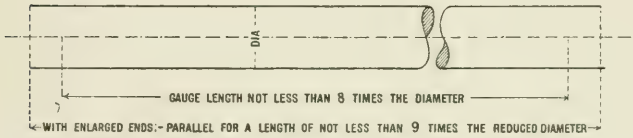


FIG. 127.—Standard tensile test-piece (France).



Test Piece A.



Test Piece B.

FIG. 127A.—British standard tensile test-piece.[1]

Test Piece B.—All test-pieces of form **B** are strictly similar, and for the same material give the same percentage of elongation. They are nearly similar to a test-piece of form **A**, 8 inches in gauge length, 2 inches wide, and ⅜-inch thick.

The following figures obtained by André Le Chatelier illustrate this effect :—

Time taken by test (seconds)		50	300	3600
Zinc wire ..	Ult. stress (tons sq. in.)	17·67	13·25	7·26
Aluminium ..	,, ,,	9·40	9·09	8·46
Copper ..	,, ,,	17·03	16·28	15·84

With zinc, the percentage elongation will vary from 1–175 per cent. according to the speed at which it is pulled out.

3. The position and direction from which the test-piece is taken must be noted (example : in the direction or perpendicular to the direction of rolling), also the condition of the metal (forged,

[1] These test-pieces are in accordance with the requirements of the Brit. Eng. Assoc.

annealed, quenched, drawn, etc.), and even the exact conditions under which this treatment was carried out: quenching temperature, time heated before quenching, temperature, size and nature of the quenching bath, etc.

4. Finally, the temperature of the test-piece during the test has an effect on the values obtained.

Below are given several examples of the actual values obtained from tensile-tests on various materials.

With steel wire, rolled and heat treated, such as aeroplane wires, the ultimate stress may attain a value of 125–160 tons per square inch, the elastic limit almost coinciding with the ultimate stress and the percentage elongation being practically nil.

Special steels, such as nickel-chrome steels, give values:

Ult. stress=95–115 tons sq. in.; E=80–100 tons sq. in.
Percentage elongation=6–10 per cent.

Rolled copper alloys:

Ult. stress=45–50 tons sq. in.; E=30–38 tons sq. in.
Percentage elongation=8–12 per cent.

Annealed copper alloys:

Ult. stress 30 tons sq. in.; E=20 tons sq. in.
Percentage elongation=25–30 per cent.

Certain high-tensile aluminium alloys recently discovered, and which are extremely interesting owing to their low specific gravity, show:—

Ult. stress=25–28 tons sq. in.; E=12–14 tons sq. in.
Percentage elongation=20–22 per cent.

Compression Tests

In the compression test, the test-piece, which is either a cylinder or a cube, is steadily compressed in one direction (one axis).

The test may be continued until the specimen fractures, the fracture usually occurring along parallel surfaces which may be perpendicular or inclined to the direction of loading.

Values for the ultimate stress and the elastic limit in compression are obtained from the test, and the definitions of these two factors are analogous to those given previously for the tensile test, the contraction being the inverse of elongation.

As a general rule, the ratio between the ultimate compression strength and the ultimate tensile strength varies from 1·4–2·0.

Compression tests are rarely required.

Bending Tests

These tests are not in general use except in the case of springs, which are subject to bending movement when in use.

The test is made on samples supported between two supports. Either the amount of deflection under a given load, the permanent deflection after subjection to a given load or the maximum load required to fracture the test-piece is measured.

Impact Tests

These tests may include bending, tensile, and compression stresses.

Obsolete Impact Tests.—Impact tests subjecting the specimen to bending stresses are only now employed. Formerly impact tests were carried out on straight bars, of definite section, placed on two supports a known distance apart. A weight fitted with a knife-edge of some definite shape was allowed to fall from a known height. Either the number of blows required to crack or fracture the specimen or the deflection produced by a given number of foot-pounds of energy formed the basis of comparison.

Tests with Notched Bars.—The above tests giving results which were not easily comparable, it was suggested that the test-piece should be notched on the side remote from the load. Tests were made with a series of bars cut from the same piece of metal which was presumed to be homogeneous: the tests were made with blows of varying magnitude by varying the length of drop of the hammer; a figure was obtained which was approximately the number of ft.-lbs. of energy necessary to fracture the specimen. The actual method used in practice consisted in fracturing the specimen with a single blow and then measuring the residual energy remaining in the hammer. This value subtracted from the total energy of the falling hammer gives the energy required to fracture the specimen. The factor or value obtained from this test is known as the impact figure (denoted by the Greek letter ρ) and is the number of ft.-lbs. of energy required to fracture the notched test-piece of definite dimensions; its value is stated in ft.-lbs.

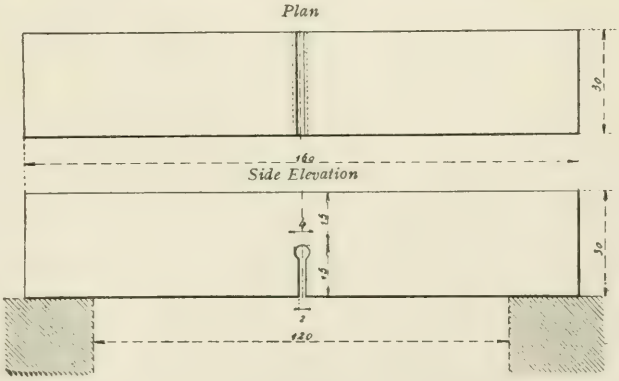


FIG. 128.—Charpy impact test-piece (large test-piece).

Types of Test-pieces.—The standard types of test-piece approved by the International Association for Testing Materials at Copenhagen (1909) are:—

The standard test-piece (Fig. 128), 30×30 mm. cross-section,

160 mm. long, the notch consisting of a circular hole 4 mm. diameter, at a tangent to the axis of the specimen, and a saw cut 2 mm. wide connecting the hole, along its length, to the outside of the specimen.

The small test-piece (Fig. 129) is a third of the size of the

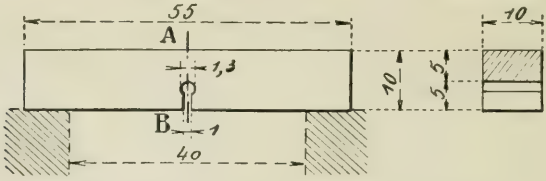


FIG. 129.—Charpy impact test-piece (small size).

standard test-piece: Cross-section 10×10 mm., length 55 mm., notch $\frac{4}{3}$ mm. diameter.

These test-pieces were designed by Charpy.

The two test-pieces are homologous, but it must be observed that the values obtained from the two sizes of test-pieces, using the same material, are not identical.

Other types or patterns of test-piece are also used. Mesnager

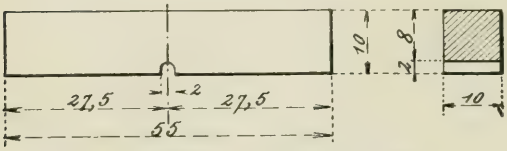


FIG. 130.—Mesnager impact test-piece.

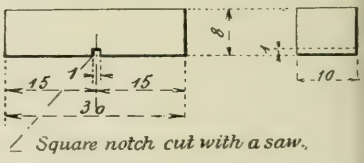


FIG. 131.—Frémont's test-piece.

type: 10×10 mm. section, 55 mm. long, notch 2×2 mm. with rounded bottom; Frémont type, 8×10 mm. section, 30 mm. long, notch 1×1 mm. with square bottom (Fig. 131).[1]

Impact Testing Machines.—The machines designed for impact tests of notched bars are of three varieties. The working principles of these three will be described.

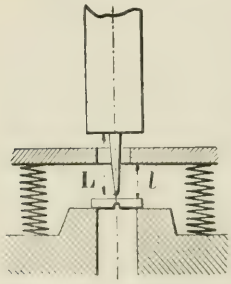


FIG. 132.—Principle of Frémont's machine.

Frémont's Machine (Figs. 132, 133).—A plate or platform, provided with a hole in its centre to allow the knife-edge which projects from the end of the hammer to pass through, is supported on coil springs. The hammer falls from a height of four metres and is supported in vertical guides.

The knife, projecting from the end of the hammer, is of such a length that it passes through the hole in the

[1] Comparisons of proportionately dimensioned specimens do not appear to be possible with impact tests. Impact test figures are of no value unless the shape and dimensions of the test-piece and notch are also stated (Charpy and Cornu-Thenard, *Revue de Metallurgie*, March–April, 1917).

plate and fractures the test-piece before the hammer touches the spring plate.

The knife therefore prevents contact with the plate until the specimen is fractured, when the plate receives the residual energy

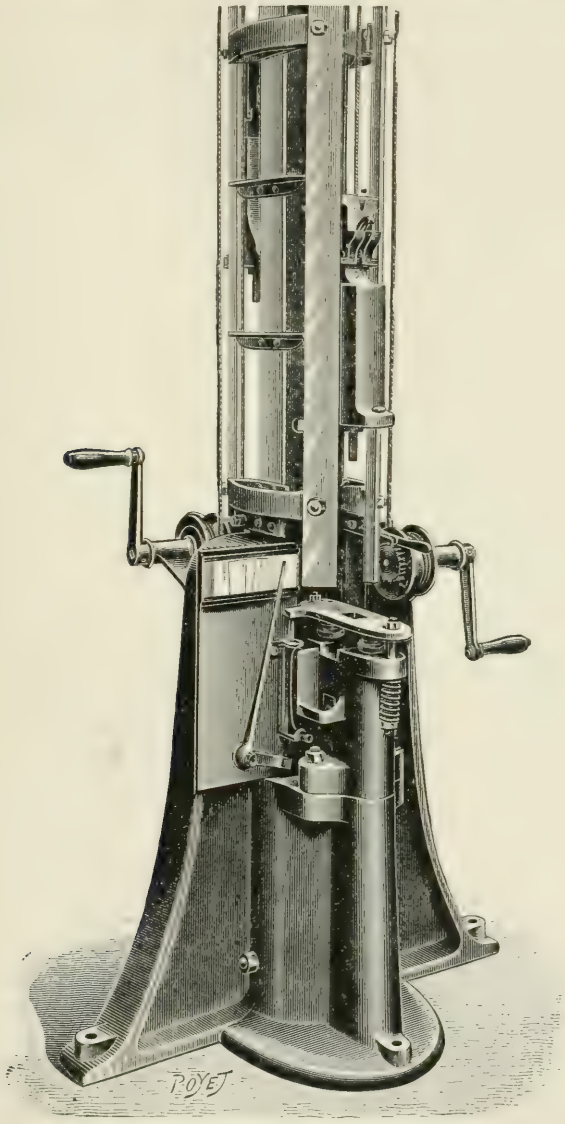


FIG. 133.—Frémont's impact testing machine.

remaining in the hammer. Suitable levers, etc., enable the movement of the spring platform to be measured, and the scale is calibrated to read the residual energy in the hammer. The original total energy being known (10 or 15 kilos falling from a height of 4 metres) the energy taken by the fracture of the

test-piece can be calculated and the impact figure is then easily deduced.

Centrifugal Impact Testing Machine (Figs. 134–136 *cont.*).—The machine consists, essentially, of a flywheel, rotated by hand, fitted with a wedge, which is brought into contact with the specimen when the flywheel has attained a definite speed. The wedge projects from the edge of the flywheel and fractures the test-piece, which is supported on an adjustable plate. The fracture of the test-piece slows the flywheel, and the diminution in speed serves as a means of measuring the amount of energy required to fracture the test-piece. The retardation is measured

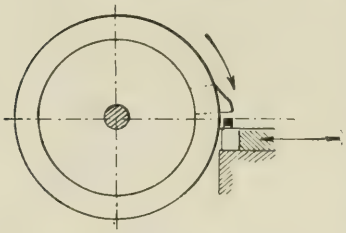


FIG. 134.—Principle of the centrifugal impact testing machine.

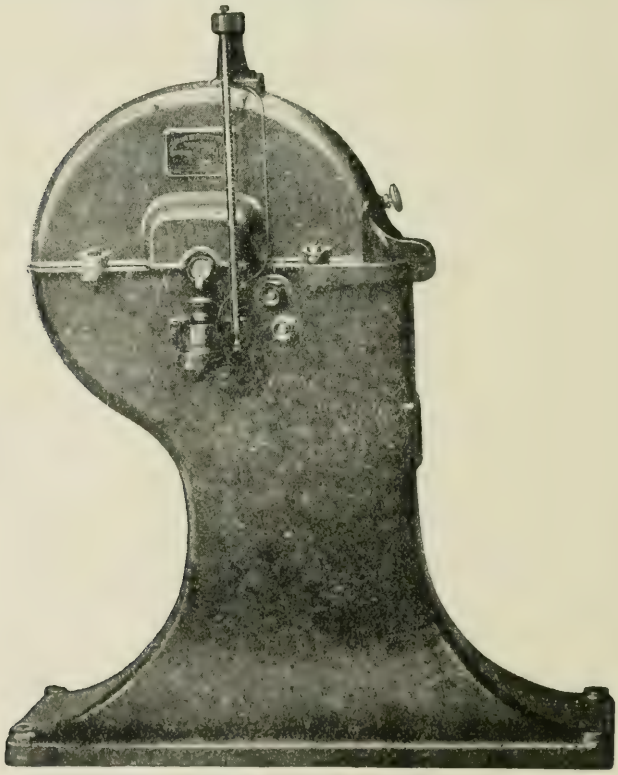


FIG. 135.—Guillery's impact testing machine.

by the variation in height of a manometer column registering the supply pressure of a pump, with closed delivery, fixed to the flywheel itself.

A machine recently constructed for the Société Française de

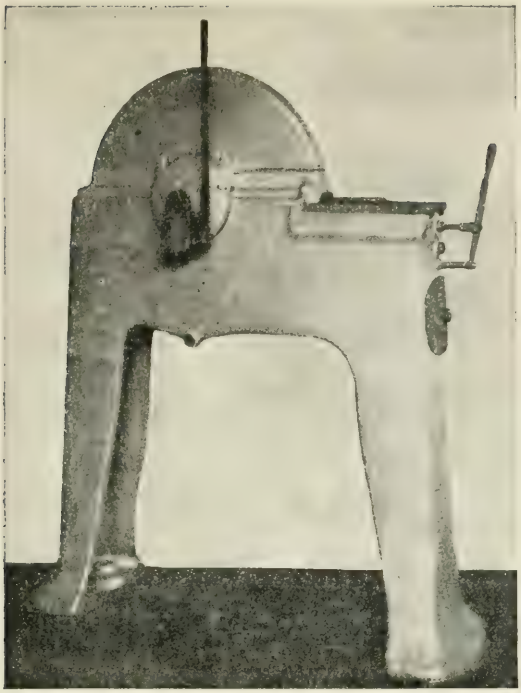


FIG. 136.—Cail rotating impact machine.

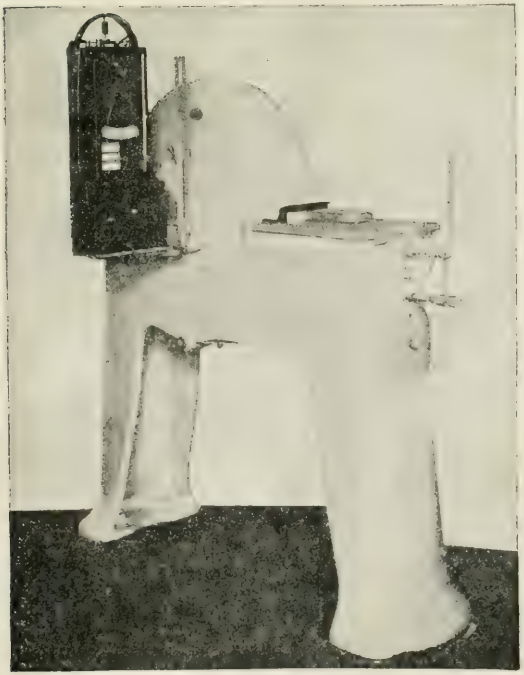


FIG. 136, *continued*.—Cail recording impact testing machine.

Constructions Mecaniques (Fig. 136 *cont.*) to test specimens 30×30 mm., is fitted with a recording apparatus consisting of a small dynamo which is driven by the flywheel.

Guillery has designed an apparatus which permits the specimen to be fixed in position (Fig. 135); the knife or wedge is held in a recess in the flywheel until the correct flywheel speed is reached, when, by pressing a button, the wedge is released by a spring and fractures the specimen.

Pendulum Impact Testing Machines (Figs. 137–139).—The machine of this type designed by Charpy consists of a heavy pendulum which swings freely between two supports. The end of the pendulum is provided with a wedge-shaped knife, fitted in a recess, which fractures the specimen.

The specimen is placed in a fixed position at the base of the machine, in the path of the pendulum, and is supported at both ends. The pendulum is released from a fixed support and after fracturing the specimens swings to a height which varies according to the amount of energy required to fracture the test-piece. At the bottom of its swing, the pendulum, in falling, picks up a small pointer which records the height the pendulum reaches, after fracturing the specimen, on a graduated scale. The impact figure is obtained from this reading by reference to a table supplied with the machine.

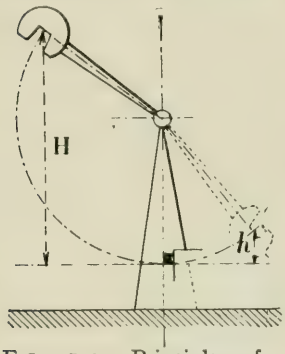


Fig. 137.—Principle of Charpy's impact testing machine.

The machine is made in three sizes according to the weight and distance of swing of the pendulum. None of these machines has, as yet, been adopted as standard.

Precautions to be observed in carrying out Impact Tests.—Many factors have a great effect on the values obtained from the test, amongst which may be cited :—

The angle of the knife or hammer.

The shape of the anvil or support on which the specimen is fixed.

The speed of impact (this point is discussed).

Finally, the effect of temperature is more appreciable than in the tensile test.

Charpy and Cornu-Thénard have suggested a method of calibration based on the measurement of the deformation of plain specimens (*Revue de Met.*, "Memoires," vol. x., p. 1233, 1913).

According to recent research by Charpy and Cornu-Thénard (*Revue de Met.*, vol. xiv., p. 84, 1917), different types and sizes of impact-testing machines will give practically identical results if the distance between the supports and the shape (curvature) of the

FIG. 138.—Charpy's impact machine. (Small model.)

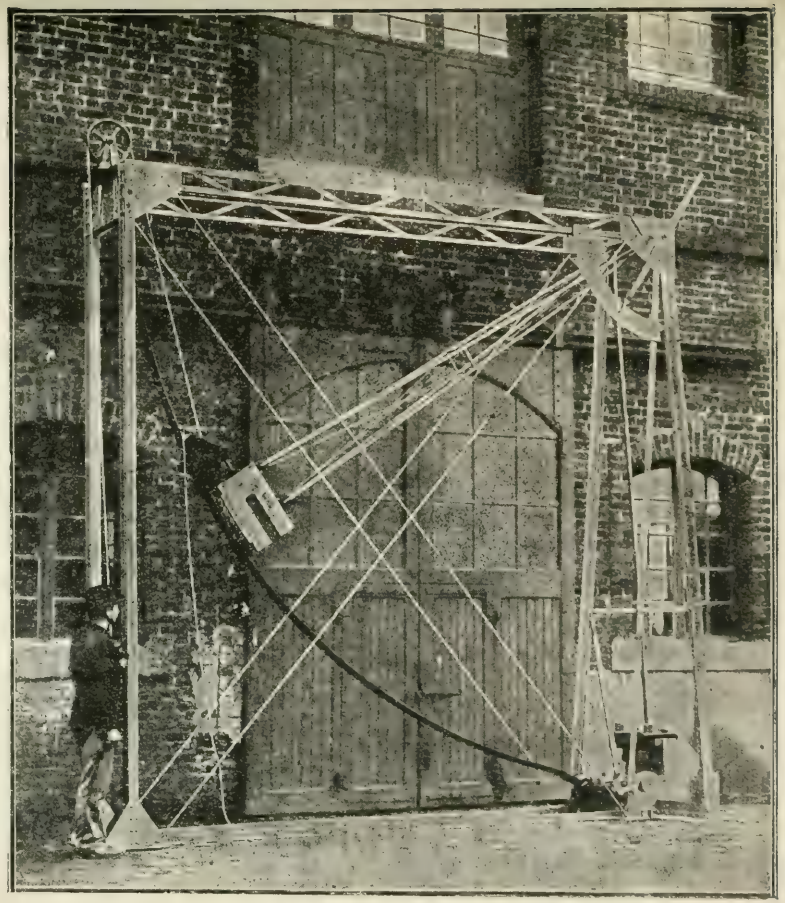


FIG. 139.—Charpy's impact machine. (Large model.)

support in contact with the specimen during fracture are made uniform.

Results of Impact Tests.—The results given by impact tests are extremely interesting, as they provide information on one of the most important defects of metallurgical materials, a defect which is not shown by any other test, namely, *brittleness*. It is possible to mention many metallurgical products which give high values for the percentage elongation and percentage reduction of area by the tensile test but which possess very low impact figures.

The difficulty of adopting the impact test as a standard test has been the fact that the figures obtained are only comparative within certain narrow limits.

It may be stated that the maximum value obtained with the large Charpy test-piece is approximately 60 kilogram-metres (400 ft.-lbs.), the minimum value being obviously 0 kilogram-metres; for most material subjected to shock, a Charpy impact figure of 10–12 kilogram-metres (70–80 ft.-lbs.) would appear to be satisfactory. In certain cases lower figures may be accepted. Thus the steel frequently used for automobile gear wheels has a figure from 5–7 kilogram-metres (35–50 ft.-lbs.) in the condition in which it is used. Again, the leaves of automobile springs give a similar figure in the direction in which they bend (along their length), but give a zero or very low reading in the direction at right angles.

Further, it must be observed, as in the case of the tensile test, that the position and direction from which the test-piece is taken materially affect the values that will be obtained and these figures will only be comparable when the conditions are identical.

Hardness Tests

Osmond defined hardness as the resistance to penetration.

The hardness of an alloy is, therefore, not a definite value but depends on the method of determination.

Methods of determining Hardness.—In commercial practice three methods are in use for the determination of hardness; the Martens' scleroscope, the Brinell hardness test, and the Shore scleroscope. It should be added that the first is a delicate laboratory test, whilst the third, a very simple operation in itself, has not been so satisfactory as was at first expected, owing to the multiplicity of factors affecting the readings.

Martens' Method of Measurement.—The essential part of the Martens' scleroscope consists of a needle or pointer terminated at one end by a diamond. An impression is made in the material by this diamond under a given definite pressure and the width of the scratch produced is measured. The scratch is but a few microns

wide and the method is therefore only suitable for laboratory tests.

Another method of using the instrument is to vary the pressure and thereby determine the minimum pressure required to produce a scratch on the test-piece.

Shore's Method of Measurement (Fig. 140).—In the case of the Shore scleroscope, which is a comparatively modern instrument, a miniature hammer fitted with a hard point (sapphire, or hard steel) is allowed to fall on the specimen from a definite height of approximately 10 inches, and the rebound is measured. The hammer falls through a small graduated glass tube and it is lifted, by suction produced by means of an indiarubber bulb, to its release position,

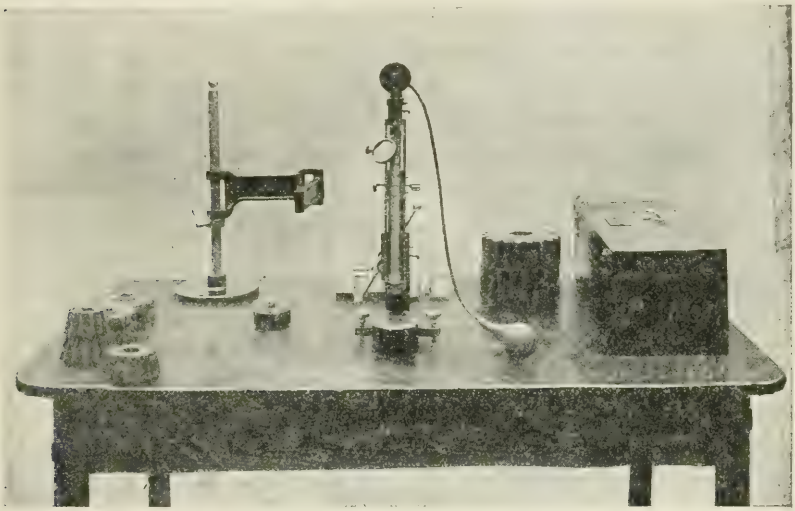


FIG. 140.—Shore scleroscope.

where it is retained by small hooks, also pneumatically operated by the same bulb. It is admitted that the rebound is dependent on the superficial hardness, but it depends, not only on the hardness, but also on the mass of the specimen and the condition of its surface. This method, which possesses enormous advantages, mainly with regard to speed of operation and absence of damage to the articles, requires great care in its use.

The accuracy of the results will obviously depend on the horizontality of the surface of the specimen, and also, more particularly, on the finish of this surface, quenching flaws, the number of rebounds on the same spot, mass of the article tested, etc.[1]

Brinell's Method of Measurement (Fig. 141).—Brinell's method of hardness testing dates from 1900; it is in general use for

[1] See Portevin and Berjot, *Rev. de Met.*, vol. vi. p. 61, 1910.

commercial tests. The principle employed is as follows: A very hard ball (quenched chrome steel ball) is pressed under a known pressure into the material to be tested, the two surfaces of the test-piece having previously been made approximately parallel. Under the given load, the steel ball of definite diameter (usually 10 mm.) makes a circular curved depression. The diameter of the depression at the surface of the test-piece is easily measured and from this is calculated the area of the depression $=a$; the load P being known, the hardness number Δ is given by the equation

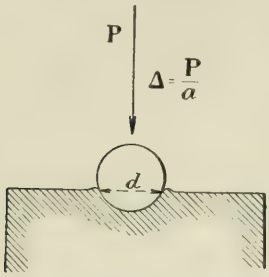


FIG. 141.—Principle of the Brinell hardness test.

$$\Delta = \frac{P}{a}$$

It will be noted that the softer the metal the greater the value of a and the lower the hardness Δ. Numerous researches have been made on this method of hardness testing.

These researches have shown the relationship existing between the hardness numbers obtained from the same sample of material using different loads, the other conditions being identical.

Bénédicks, in his research on carbon steels (1904), proposed the following formula:—

$$\Delta_0 = \Delta \frac{l + P_0}{l + P} \sqrt{\frac{D}{D_0}}$$

Δ_0 being the Brinell hardness number, obtained with a load P_0 and a ball of diameter D_0, and Δ the Brinell number with a load P and a ball of diameter D. In this formula the value of l is dependent on the value of P; it can be determined experimentally within certain limits.

The Brinell test is extremely interesting because of the relationship that has been found to exist between the Brinell number Δ and the ultimate strength R of any material.

In many cases this relation corresponds to an equation:

$$R = C \times \Delta$$

C being a constant which has to be determined for any given material and which has been accurately determined in the case of annealed carbon steels and found to equal 0·35 (mean value).

The value of C also varies with samples of the same material tested in different directions (direction of rolling, etc.). In a recent research (*Revue de Met.*, vol. viii., "Memoires," p. 251, 1911), M. Grard has given the results of very accurate determinations of the value of C for certain steels. He has found:

	Values of C for tests.	
	Perpendicular to the direction of rolling.	Parallel to the direction of rolling.
Extra-mild steel ($\Delta < 120$)	0·360	0·345
Mild steels ($120 < \Delta < 160$)	0·355	0·342
Medium carbon steels ($160 < \Delta < 180$)	0·353	0·337
Hard steels ($\Delta < 180$)	0·349	0·321

In the case of copper and annealed brasses, C = 0·50.[1] This relationship cannot be generally applied. Thus, as a typical example, it is not possible to compare copper in the annealed state and after varying amounts of cold-work.[2]

Moreover, it must be observed that the hardness numbers are not to be relied upon when they exceed the value 500. This is no doubt due to the deformation that the steel ball itself must undergo during the test on such hard materials. Many alloys *as cast* give irregular impressions. This is due to the mechanical anisotropism of the particles of solidification.[3]

Certain precautions are necessary if the results obtained from Brinell hardness tests are to be comparable with each other. The metal to be tested must always be in the same state (annealed, etc.). Further, it is advisable to remove the outside skin from the test-pieces as this may change during annealing (decarburisation of steels).

Finally, it is necessary to allow the load to remain on the test-piece a sufficient time to give a complete impression and also to note that the impressions are sufficiently far apart for the work-hardness produced by the impressions not to interfere with the successive readings.

Below is given a list of Brinell numbers for typical metals and alloys; these alloys, if not otherwise stated, have been rolled and annealed; the tests were made with a load of 3000 kilos and a ball 10 mm. diameter.

Extra-mild steel	110
Medium carbon steel	170
Hard steel	315
Bronze: Cu 90, Sn 10 cast	80
,, Cu 84, Sn 16 cast	117
Brass: Cu 90, Zn 10	52
,, Cu 80, Zn 20	54
,, Cu 70, Zn 30	56
,, Cu 65, Zn 35	58
,, Cu 62, Zn 38	70
,, Cu 60, Zn 40	80
,, Cu 58, Zn 42	90
,, Cu 58, Zn 40, Pb 2	84
Aluminium Bronze: Cu 95, Al 5	80
,, Cu 90, Al 10	120
Cupro-Nickel: Cu 90, Ni 10	44
,, Cu 80, Ni 20	47
Cupro-Nickel-Aluminium: Cu 83, Ni 15, Al 2	191

[1] Guillet, *Revue de Met.*, "Memoires," p. 1115, 1914.
[2] Guillet, *Revue de Met.*, "Memoires," p. 819, 1915.
[3] Portevin, *Revue de Met.*, "Memoires," p. 95, 1915.

There are three types of machines in use for Brinell hardness tests:

The weighted lever machines, which are the simplest, the most constant, and the easiest to adjust; those in which the pressure or load is produced by a small hydraulic press, the pressure being read on a graduated gauge; those working at a fixed pressure which is produced by springs which are compressed by a definite load.

In the first class are included the Léon Bollée and Dérihon machines; in the second, those of the Aktiebolaget Alpha; in the third, the machines produced by Guertler and the Société française de constructions mécaniques.

Martens and Heyn have suggested the measurement of the depth of the impression as an alternative method to the measurement of its diameter. In machines arranged for this form of measurement the load is applied from below and three small pointers rest on the specimen outside the area affected by the impression. The ball remains stationary and the test-piece moves upwards as the impression is formed. The three pointers operate a small piston which, in turn, regulates the height of a mercury column in a small graduated capillary tube. The depth of the impression is read direct from the graduated tube.

It may be mentioned that there is not in every case a definite connection between the Brinell hardness number and the machining qualities of any material. The most typical example of this kind is given by the high nickel steels which are extremely difficult to machine, but which have a hardness number of only 120. A large number of cast alloys, especially those containing hard metals (bearing metals, hard bronzes, etc.), give very irregular impressions.

The other mechanical tests to which metallic products may be subjected, such as bending, shearing, punching, torsion, and impact tests, may be considered as alternative works tests of less importance than those described. They will not be included in the present description, which is intended merely as an outline of the most general tests used in commercial practice as a guarantee of the quality of the material.

RELATION BETWEEN THE MECHANICAL PROPERTIES AND THE CONSTITUTION

The connection between the mechanical properties and the constitution of metals and alloys will now be described. The general principles must first be considered.

1. There is a definite relation between the crystal grain size and the mechanical properties, chiefly brittleness, which increases, other conditions being constant, with the size of the grains. However,

Stead has stated that it is possible for an alloy consisting of small grains similarly oriented to be more fragile than one consisting of larger grains.

2. All compounds, whether formed on passing from the liquid state, or due to a secondary reaction occurring in the solid state, are brittle and usually hard.

3. A solid solution corresponding to a maximum of the liquidus exhibits the same properties, which tends to confirm the opinion of Tammann that such a solution is formed by a compound dissolving.

4. A solid solution, approximating to a pure metal, exhibits certain mechanical properties analogous to those of the metal. If the metal is ductile, the solution will also be ductile, while if the metal is brittle, the solution will exhibit similar properties. This difference n the properties of definite compounds and solid solutions may be due to the fact that in general the first solidify as regular convex crystals, and the second as a mass of interlocking dendrites or tree-like structures.

It is possible from these principles, determined from experience, to deduce certain interesting rules.[1]

If the equilibrium diagram shows the two metals as entirely miscible, the mechanical properties of the alloys of the system will vary continuously from those of the one metal to those of the other metal. It is therefore possible to infer that a diagram, in which the liquidus consists of a single branch of a curve without transformations in the solid state, can only be formed by two metals whose mechanical properties are not opposed ; thus a malleable and a non-malleable metal are not completely miscible in the solid state, but two malleable metals (gold and silver) or two non-malleable metals (antimony and bismuth) may be miscible in all proportions in the solid state.

If the two metals give a diagram which indicates that they are deposited side by side in the different alloys formed, giving rise to a eutectic, three cases are possible :—

1. The two metals are malleable (the properties of the metals at ordinary temperatures are here considered) ; then all the alloys will be malleable.

2. The two metals are not malleable ; none of the alloys are malleable.

3. One metal is malleable, the other non-malleable ; the alloys will be malleable up to the eutectic concentration.

Moreover, it should be observed that a non-malleable metal only seriously affects the properties of the alloy when it occurs in the free state, which is not considered the case when it is present as fine lamellæ in a eutectic.

[1] Guillet.

The shape of the particles also affects the mechanical properties, as shown by the cementite needles tending to increase the brittleness of steels.

Further, Kurnakow and Zemczuzny have put forward the following conclusions, deduced from the study of metals forming solid solutions :

1. The formation of solid solutions is accompanied by an increase of hardness as compared with the hardness of the components.

2. In the case of two metals completely miscible in the solid state, the variation in hardness as a function of the concentration is shown by a continuous curve with a maximum. This maximum value corresponds with the minimum electrical conductivity as previously described (see p. 59).

3. With a mechanical mixture of two constituents, the hardness is a linear function of the chemical composition.

4. With metals partially soluble in the solid state, the limits of miscibility are indicated as a break in the curve in which the hardness is plotted as a function of the concentration.

Also the diagram showing the hardness as a function of the chemical composition is the inverse of that showing the electrical resistance as a function of the chemical composition (see p. 59).

Further, it may be stated that, for most purposes (bearings and frictional materials excepted), the best mechanical results are obtained from any alloy when its structure is as homogeneous as possible, either as cast, or after further treatment. Henry Le Chatelier has stated, " The best result is obtained when the microscope shows nothing."

It must be noted that certain structures indicate well-defined properties : the martensitic structure met with in many quenched materials is characteristic of the maximum state of hardness of any material ; the presence of a definite compound denotes good frictional properties in proportion to the content of these crystals.

Finally, if the structure consists of two constituents, the mechanical properties are proportional to the amounts of the respective constituents present. A special example of this type will be mentioned in a later chapter when considering the apparent compositions of certain special copper alloys ; the chemical composition, in these cases, giving very little information as to the mechanical properties, a microscopical examination must be made.

It must be clearly understood that, in examining the equilibrium diagram of binary alloys, there will be found areas consisting of one constituent (solid solutions) and areas containing two constituents (two metals, one metal and a solid solution, one metal and a compound, two solid solutions or two compounds). It has been

previously stated that, in an area consisting of one constituent, no direct relation exists between the mechanical properties and the constitution.

In an area containing two constituents, it appears certain that the law of proportionality will apply, and that any property will vary according to a straight line connecting the values of this property possessed by the respective constituents. But it has been shown that the size of the structure also affects the mechanical properties. Two cases will be considered: the two constituents either do or do not form a eutectic or eutectoid. If they do not form a eutectic or eutectoid, the other conditions being constant (more particularly the mechanical and heat treatments), the law of proportionality will apply. If the eutectic is formed it may possess certain distinctive properties, such as exceptional hardness, etc. The rule of proportionality will now apply not between the constituent metals, but between the eutectic and the one constituent, and again between the eutectic and the other constituent.[1]

Various Treatments to which Metals and Alloys are subjected and the Effects of such Treatment on the Mechanical Properties

Metals and alloys are subjected to various treatments to enable them to satisfy two main conditions:

1. That they may have a suitable form or shape for commercial use.

2. To impart certain definite qualities.

Such treatment may be classified under three headings:

(1) Mechanical treatment, which satisfies both the requirements above mentioned, consists in working the metal at atmospheric or higher temperatures, the correct temperature being dependent on the metal.

There are many forms of mechanical treatment. The chief are; forging, rolling, swaging, solid-drawing and wire-drawing, but stamping, die-stamping, etc., may be added.

(2) Chemical treatment, the object of which is to modify the mechanical, physical, or chemical properties of the original material by chemical means.

The principal forms of chemical treatment are: cementation (case hardening), dipping and electro-depositing, soldering and brazing.

(3) Heat treatment, in which only the temperature of the metal

[1] The maximum relative hardness of the eutectic alloy is destroyed by suitable annealing; this has been demonstrated by Glasunow and Matweieff in the case of the cadmium-zinc series. Thus it is possible, by coalescence (p. 77), to re-establish the direct relationship between the hardness and the proportions of the constituents (see Portevin and Bernard, "The Effect of Coalescence on the Mechanical Properties of Alloys," *Revue de Met.*, vol. xii. p. 143, 1915).

is changed and the object of which is to impart certain definite qualities to the material. The various types of heat treatment are known as quenching, annealing, tempering; the last being a special form of annealing.

Autogeneous welding might possibly be regarded as a type of heat treatment.

Finally casting, which consists in allowing a molten metal to solidify in a mould of definite shape, precedes both thermal and mechanical treatment.

Mechanical Treatment

This subject will only be dealt with in the present volume as regards the alterations that occur in the structure and the mechanical properties of the metal.

Cast Metal.—Consider first of all the cast metal, as it leaves the foundry. It matters little whether it is an ingot for the rolling mill or a definite casting which will be used without further mechanical treatment.

It has been shown (pp. 70 and 74) that the rate of solidification and the subsequent rate of cooling affect the structure of alloys and consequently the mechanical properties.

The rates of solidification and cooling depend on the casting temperature, the size of the ingot or casting, the temperature of the mould, the material from which the mould is made (sand or metal-chill castings). It is possible by variation of these factors to modify the physcio-chemical condition of the alloy—grain size, etc.

By such variations it is possible with the same pig iron to obtain the stable conditions of equilibrium-graphite (grey cast iron), or the labile equilibrium-cementite (white iron, see p. 133), in which case, with the same carbon content, all the mechanical properties are changed; a practical application of this is found in the manufacture of chill cast rolls for rolling mills which have an outer surface of extremely hard white iron.

If the alloy consists of two or more constituents, the particles of solidification of each constituent increase in size as the solidification becomes slower. The bearing metals may be taken as a typical example; their frictional qualities depend on the formation and size of the crystals of the compounds SbSn and Cu_3Sn (see Chap. V., p. 250).

In the case of a solid solution, the rate of cooling affects firstly the chemical homogeneity of the solid solution, and secondly the size of the crystal grains. Since any further transformations are dependent on this granular structure, the effects of this structure are evident even after such transformations (cellular or network structure or Widmanstaelten structure), and consequently exert an

influence, even in this case, on the mechanical properties of the material, creating in this manner a type of hereditary effect due to the original solidification. In the following tables are given some typical examples of the effect of varying casting temperatures on the properties of certain alloys. The figures are quoted from researches carried out by Longmuir.

1. Bronze: Cu=88, Sn=10, Zn=2.

Casting temperature.	Ult. stress (tons sq. in.).	Elastic limit (tons sq. in.).	Percentage elongation (100 mm.).	Percentage reduction in area.
1173° C.	8·33	6·44	5·2	14·3
1069° C.	14·76	8·46	14·5	16·7
965° C.	10·98	8·96	5·0	6·4

2. Brass: Cu=65, Zn=35.

Casting temperature.	Ult. stress (tons sq. in.).	Elastic limit (tons sq. in.).	Percentage elongation (100 mm.).	Percentage reduction in area.
1182°	11·48	4·35	37·7	37
1020°	12·62	3·91	43·0	35
850°	7·38	3·91	15·0	15

The effect of annealing on cast material will be described later.

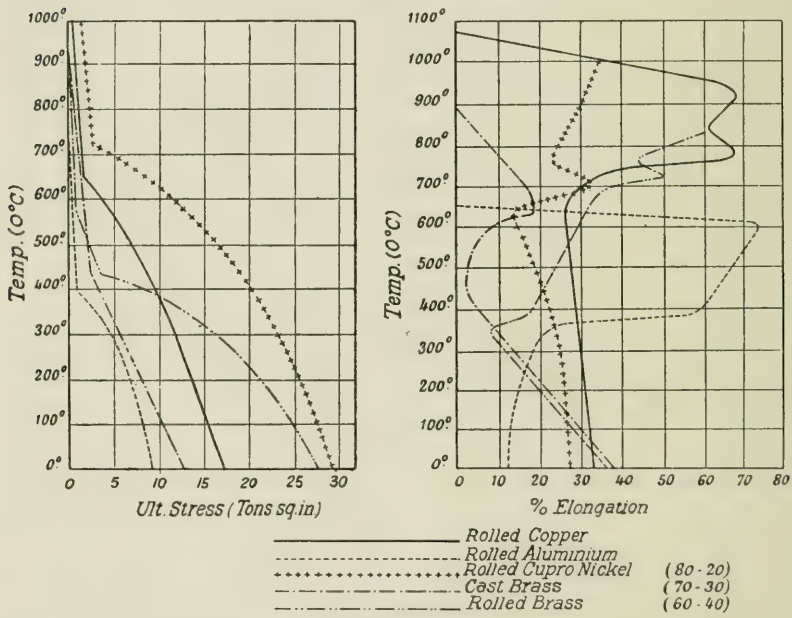
Forged or Rolled Metal.—The case of an ingot that has been forged will now be considered. The forging may have been performed either with a steam-hammer, a hydraulic press, or in the rolling mill. It is recognised that rolling tends to create an elongated structure and therefore the material will be stronger in one direction (see Chap. VI., Macrostructure of Steels). It has always been the accepted view of metallurgists that the hydraulic press gives superior results to the hammer; but, Charpy's interesting researches appear to prove that the method of forging has very little effect on the qualities of the material (Génie civil, 17 fév., 1917). The forging temperature is the most important consideration; the operation may be performed at atmospheric temperature or at higher temperatures; but, in any case, the temperature must be below that of the solidus, otherwise, during the operation the liquid portion of the alloy would be squeezed out of the ingot.

As a general rule, the temperature at which the material is most ductile is chosen. However, certain metals such as lead, aluminium, and iron can be rolled both hot and cold; consequently, the type of work, the finish required, etc., will be the deciding factors as to whether hot or cold rolling will be the method employed. It is therefore necessary, in order to determine the best rolling temperature, to

know the effect of change of temperature on the properties of the material. Many recent researches have been undertaken to determine these variations. A few of the results obtained are given by the curves Figs. 142, 143.

It will be seen that, with copper, the ultimate stress decreases with rise of temperature, being very low in value above 650°, whilst the percentage elongation, which remains fairly constant up to that temperature, increases greatly in value between 750° and 1000° C. Again, the ultimate stress of aluminium becomes very low at 400° and the percentage elongation increases tremendously between

Variations in the Ultimate Strength and % Elongation with change of Temperature.



FIGS. 142, 143.

400° and 600° C. Cupro-nickel containing 80 per cent. Cu has a very low ultimate stress above 700° C., whilst the percentage elongation increases above that temperature; brass, containing 70 per cent. copper, has very low ultimate stress and percentage elongation at 400° C., and since the elongation only increases between 600° and 700° C. the temperature limits are too close to permit of hot rolling, whilst brass containing 60 per cent. copper, which has the same ultimate stress as the previous alloy, has a much greater percentage elongation above 400–500° C., and is therefore suitable for hot rolling.

In several instances metals and alloys which it is impossible or extremely difficult to roll in the cold are easily hot rolled. Zinc is

a typical example of such a metal; extremely brittle at ordinary temperatures it can be easily rolled at 125° C. Examples of alloys of this type are: brasses containing between 57 and 63 per cent. copper, and steels containing more than 0·2–0·3 per cent. C.

The connection with the equilibrium diagram is very clearly shown in this case. At ordinary temperatures these alloys contain a non-malleable constituent which, on heating above the transformation temperature, is converted into a malleable constituent. It is obvious that with these alloys the temperature, during forging operations, must be maintained above the transformation temperature if cracks in the metal are to be avoided. It is not only alloys with transformation points which may or should be forged at high temperatures, but, the properties of certain materials change with alteration of temperature in such a manner that they are only workable at definite temperatures. The comparative curves for copper and aluminium (Figs. 142, 143) indicate that the operation of rolling will be more easily performed at 800° C. for the former and 400° for the latter, than at atmospheric temperature.

If any material is to be worked commercially, at a high temperature, it is essential that the material shall possess the property of a high percentage elongation over a comparatively wide range of temperature, which is not the case with 70 Cu : 30 Zn brass.

The connection which exists between the equilibrium diagram and the suitability of the material for cold rolling has already been mentioned, but experience seems to justify the further statement that the only alloys suitable for cold rolling are solid solutions approximating to pure metals that can be cold rolled and alloys containing a very small quantity of any non-malleable material at atmospheric temperature (very mild steels).

As regards the alterations to the properties and structure of the material, there is a marked difference between cold and hot rolling. From the practical point of view the two methods of treatment are entirely different. The speed of the rolls is very much slower for cold rolling than for hot rolling (in the case of brass: 40 revs. per minute instead of 200). The rolls in a cold-rolling mill are of very much larger diameter than those used for hot rolls (for brass rod: 18 ins. instead of 8–12 ins.). The process of cold rolling bars is carried out by reducing through flat plates and round passes; while, in hot rolling, the rolls are fitted with oval and splayed circular passes. Moreover, the method of working is quite different; for with cold rolling, it is necessary, owing to the hardening effect produced, to anneal the metal after several passes through the rolls, whilst in hot rolling only one heating or

at most one or two reheatings are required before the material is in the finished state. Further, a hot mill requires a more complicated installation as regards power and labour than a cold mill.

The question of the properties and structure of the material will now be further considered.

The first effect of rolling is to destroy the structure of the cast metal, by deforming and breaking down the crystal grains. Hot-rolled metal is usually more evenly affected throughout the mass than cold-rolled metal. The reservation *usually* is added, as certain exceptionally malleable metals, for example, lead,[1] are similarly affected by either treatment. Moreover, cold-work produces a much greater hardening effect than hot-work; but, the effects of cold-work (hardening, strains, etc.), consisting of modifications of the properties of the material due to permanent deformations, disappear on heating to a comparatively high temperature (annealing). Therefore, if the work producing this deformation is carried out at the annealing temperature, the hardening effect will be practically nil. It appears that work hardness is brought about by the deformation of the grains along internal moving surfaces or *gliding planes*.

Beilby has given the further theory that the work-hardness is due to an amorphous layer of material formed between the crystals. In any case, the work-hardened material, when viewed under the microscope, shows the crystal grains to have been distorted and if the amount of cold-work has been sufficient these grains will have disappeared.

Drawn Metal.—If material is examined that has been subjected to the other forms of mechanical work in the cold, producing greater deformation than rolling or forging, the effects of work-hardness will be far more evident.

Wire-drawing is a particularly good example of this type of treatment, as it consists in drawing the material through a series of dies of decreasing cross-section. The die regulates the size and shape of the finished product and frequently imparts a very high polish to the material. Such treatment, if carried out at ordinary temperatures (usual practice), gives rise to considerable work-hardness in the material, and the crystal grains are therefore considerably deformed.

The data tabulated below enable the effects of such treatment to be appreciated: rolling improves the mechanical properties of cast metal, renders it more homogeneous and lessens the physical defects; this is shown by the increase in the ultimate stress, elastic limit, percentage elongation, and impact figures.

[1] Lead undergoes spontaneous recrystallisation at ordinary temperatures.

DETERMINATION OF THE ELASTIC LIMIT BY FRÉMONT'S METHOD.

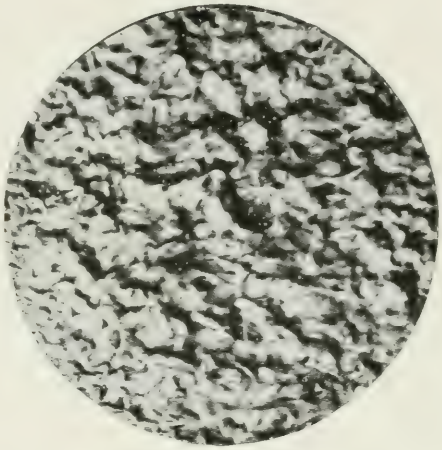


FIG. 125.—Test-piece polished and deformed.

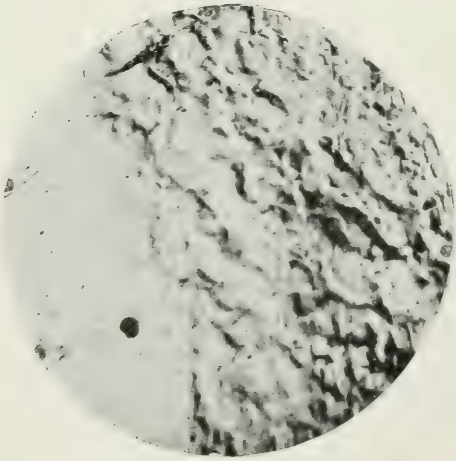


FIG. 126.—Portion of test-piece situated at the extremity of the deformation.

RECRYSTALLIZATION OF COLD ROLLED ALUMINIUM.

(H. Le Chatelier.)

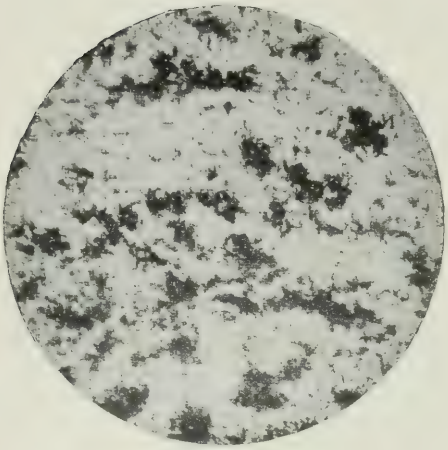


Fig. 144.—Aluminium unchanged.
(× 200.)

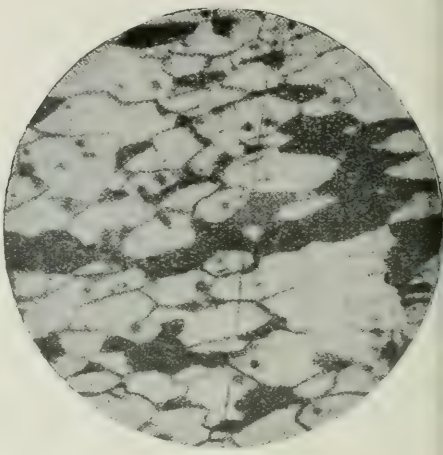


Fig. 145.—Recrystallized aluminium.
(× 200.)

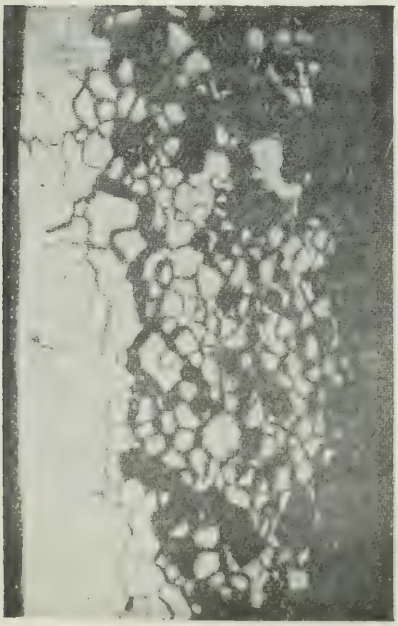


Fig. 146.—Recrystallized aluminium.
Unetched.
(× 50.)

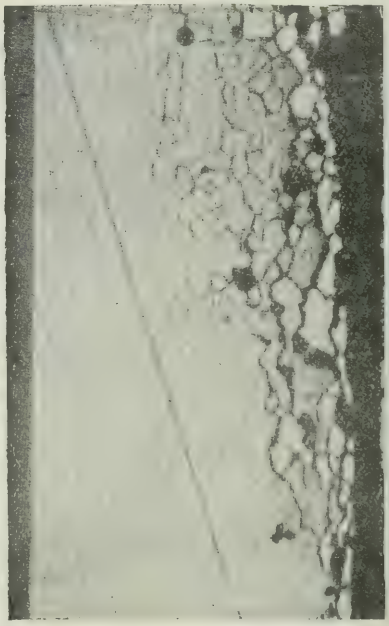


Fig. 147.—Recrystallized aluminium.
Slight electrolytic etching.
(× 50.)

Examples (the figures for rolled metal are for metal that has been annealed after rolling in order to remove work-hardness, etc.) :—

	Ult. stress (tons sq. in.).	Percentage elongation.
Cast steel	26·50	22
,, rolled	28·40	26
Special brass, cast	23·35	25
,, rolled	28·40	30
Aluminium, cast	6·31	8
,, rolled	7·57	15
Copper, cast	?	?
,, rolled	13·88	50

It will be observed that no figures are given for cast copper as it is practically impossible to cast the metal in a sound condition.

If rolled metal is subsequently drawn there is an increase in the ultimate stress and a very marked increase in the elastic limit, at the same time the percentage elongation and the impact figures are decreased.

The following tests were all carried out on round bars 22 mm. diameter after rolling, and 20 mm. diameter after drawing :—

	Ult. stress (tons sq. in.).	Elastic limit.	Percentage elongation.	Impact figure.
Annealed steel	23·03	16·72	27	32
,, ,, drawn	29·09	22·27	14	10
Annealed brass	23·15	8·39	40	7
,, ,, drawn	27·82	26·56	21·5	5
Annealed nickel silver, 10% Ni	10·29	1·7	40	14
,, ,, drawn..	12·33	10·29	14	8

The large increase in the elastic limit caused by cold-working will be noticed, especially in the case of nickel-silver.

The alteration in the mechanical properties is not the only effect produced by cold-work—the chemical properties are also affected; with but few exceptions, other conditions being constant, cold-worked metals are more readily attacked than the same metals in the annealed state.

Recent research by Henry Le Chatelier and also by Heyn and Bauer has shown that cold-worked aluminium may disintegrate rapidly without chemical change. Aluminium possesses a very marked network or cellular structure and the change occurs by the separation of these cells or crystals from the mass (Pl. XVIII., Figs. 144–147).

Cohen has studied the interesting changes that occur in the metal tin and in the brasses; these changes may be explained in a different manner to the previous example. It should be recognised

that cold-worked material must of necessity be irregular in its properties, owing to the enormous internal strains produced,[1] and that subsequent annealing, in certain instances, is liable to produce injurious effects (to be described later); such treatments should therefore be avoided whenever possible.

Heat Treatment [2]

Quenching.—*Definition.*—The operation of quenching consists in heating a metal or alloy to a high temperature and then cooling it quickly by immersion, usually in a liquid, but sometimes in a gas (air quenching), and in certain exceptional cases in a solid (fusible alloys, tallow), etc.

Object of quenching.—The object of quenching is to alter the properties of a metal or alloy.

It has been shown that variations in the rate of cooling, etc., may alter the speed of transformations occurring in certain alloys during cooling, and may even entirely prevent such transformations; in such cases, the physico-chemical equilibrium, the structure and the properties (work-hardness when the transformation is accompanied by a change in volume), etc., of the alloy are also affected. Quenching, therefore, will tend to bring about the above result, and an alloy is said to be affected by quenching when such modifications are produced in its properties. Very often such modification is evident by a marked increase in the hardness; but, in recent years, quenching (with or without subsequent tempering, according to the metal treated) has been increasingly used to improve various other properties, chiefly the resistance to fatigue. Finally, it may be observed that certain metals are softened by quenching.

Metals affected by quenching.—Quenching can be applied to metals and alloys that undergo transformations on heating. The effect of quenching such alloys is partially or totally to suppress or displace such transformations during cooling. The relation between the quenching temperature and the equilibrium diagram that defines the transformation temperature is apparent. In order that a transformation occurring during cooling may be effected it is essential that the stable condition of the metal when hot shall be different to the stable condition at ordinary temperatures.

Two conditions must be satisfied:—

1. If a metal or alloy is to be altered by quenching, it must undergo a transformation on heating.

2. The quenching temperature must be higher than the transformation temperature on heating; if the metal or alloy shows

[1] Heyn and Bauer (see p. 119).

[2] For further details refer to Léon Guillet, "Traitements thermiques de produits métallurgiques: trempe, recuit, revenu," Dunod et Pinot, editéurs.

several transformation points, and the maximum quenching effect is required, the quenching temperature must be above the upper transformation temperature on heating.

Quenching Conditions.—Two questions are immediately raised by the above principles:

1. Are all metals and alloys possessing transformation points affected by quenching?

2. Is it only necessary for the quenching temperature to be above the transformation temperature, and does quenching at varying temperatures between the transformation temperature and the solidus produce different results? (Quenching between the solidus and the liquidus, giving rise to deformation and other defects such as blow holes, segregation, etc., will not be considered.)

The answer to the first question is that the existing information shows that there are very few exceptions. For instance, certain alloys, in which the only evidence in support of a transformation existing, is a change in the magnetic properties (high nickel steels), are not affected by quenching; no matter how rapid the cooling, it has been found impossible to retain the non-magnetic state existing at high temperatures.

An answer to the second question is more difficult. It would appear, according to the present theories, that it may be accepted that the properties obtained by quenching (more particularly hardness) are due to the existence of a transitional constituent not in equilibrium, the properties of which are different to those of both the stable forms (at high and ordinary temperatures). Thus, if it were possible to retain steel in the form stable at high temperatures at ordinary temperatures, it would be more malleable instead of being of greater hardness.

Quenching, under these conditions, would be of no commercial utility.

Increasing the quenching temperature has the same effect as increasing the rate of cooling—lowers the transformation temperature on cooling. Therefore it tends to retain more and more of the stable constituent at that temperature in the stable condition; a condition which in practice is not desired. The quenching temperature should be as little above the transformation temperature as the working conditions will permit, at least with ordinary carbon steels.

The opposite effect is found with certain special steels. In this instance raising the quenching temperature lowers the transformation temperature without retaining the stable constituents; such steels (high-speed tool steels) are given a comparatively slow quenching (air quenching) from a high temperature.

Theories of Quenching.—Several theories have been formulated

to explain the increase of hardness produced by quenching, the basis being that a transitional constituent is retained in the quenched condition.

Of these theories the following may be mentioned :—

1. The theory put forward by Benedicks and Henry Le Chatelier in which the quenched constituents are assumed to exist in an extremely fine state of division or colloidal condition.

2. The theory put forward by André Le Chatelier and Grenet which ascribes the hardness as due to the internal strains (*l'écrouissage*) produced by the change in volume during the transformation on cooling when the metal is only slightly malleable.

It is quite probable that the properties of quenched materials may be due to a combination of the two theories mentioned.

Quenching Conditions.—The effect of varying the quenching temperature has already been described. The other conditions affecting this operation will now be briefly considered : [1] the period of heating, which must be long enough to enable the transformation to be complete throughout the mass ; the rate of cooling, which controls the retention of the stable form and the temperature at which the transformation occurs. The rate of cooling is dependent on several factors ; temperature, size, and nature of the quenching bath. The nature or character of the quenching bath merits further attention. The contact between the article and the bath is affected by the volatilisation of the bath during the quenching operation ; increased viscosity reduces the convection effect and decreases the quenching properties, whereas the better its conduction of heat, the greater its quenching properties.

Finally, the greater the specific heat and the heat of vaporisation of the bath, the less its temperature is raised by quenchings, and therefore the greater the amount of heat absorbed during quenching operations. Thus a bath, the constituents of which have the highest specific heats and latent heats of vaporisation, produces the greatest quenching effect.

Self-hardening Metals.—The property of self-hardening possessed by certain metals is directly due to the phenomena of thermal hysteresis which has already been described. For instance, if the transformation temperature is considerably lowered by the normal rate of cooling in air, it will only be necessary to heat the material above the transformation temperature on heating, and allow it to cool in air in order to produce the quenching effect. In such instances the effect of raising the quenching temperature is often very considerable.

Annealing and Tempering.—*Definition.*—The operation of annealing

[1] For further details refer to Guillet, "Trempe, recuit, revenu," Dunod et Pinat, Paris, 1911.

consists in taking a metal to a high temperature and allowing it to cool very slowly.

Object of annealing.—Annealing may be applied to the following materials: (1) metal, as cast; (2) cold-worked metal; (3) quenched metal; (4) overheated or burnt metal.

In the first and last cases the object of annealing is to improve the qualities of the material, more particularly to refine the structure (reduce the size); in the second case the object is to remove the work-hardness and internal strain, either to improve the machining qualities or to render the material more reliable and constant as regards the mechanical properties; in the third case the object is partially or totally to destroy the effects of quenching. If the only purpose of annealing is to remove part of the quenching effect, the operation is known as *tempering*, and is performed at temperatures below the transformation temperature. The effect on the structure produced by annealing has been dealt with in the previous chapter. There is, in every case, a tendency to bring about the conditions for physico-chemical equilibrium, as defined by the equilibrium diagram, and also crystalline equilibrium.

The annealing of Unquenched Material without passing through a Transformation Point.—Suppose the annealing operation is performed without passing through a transformation point on heating, the effect of the treatment will be to tend to bring about mechanical equilibrium, physico-chemical equilibrium, and also structural and crystalline equilibrium.

A. The improvement in the *mechanical equilibrium* will consist in the removal of the internal strains and abnormal properties produced by cold-work. Heyn and Bauer have shown that, in a 25 per cent. nickel-steel, the internal strains are reduced from +3510 to −3810 atmospheres, in cold-worked material, to +200 to −250 atmospheres, by annealing the metal for one hour at 850° C. In actual practice these internal strains are continually varied by changes in temperature, and even by superficial corrosion. It is therefore evident that their removal by annealing is of the utmost industrial importance.

B. *Physico-chemical Equilibrium.*—This is only brought about when the previous cooling has been so rapid that the material has not had sufficient time to attain equilibrium conditions.

For example, by annealing a bronze consisting of a single heterogeneous solid solution it is possible to increase the size of the Brinell impression (3000 kilos, 10 mm. ball) from 4·1 to 4·4 mm. By this means (annealing), chemically heterogeneous solid solutions due to rapid cooling become more homogeneous; diffusion occurs in the solid state, the extent of such diffusion being greater the higher the temperature. There is a proportionate change in the properties.

The effect on the mechanical properties is complicated by the fact that recrystallisation also occurs.

C. *Structural Equilibrium.*—This brings about the coalescence of the individual particles of an alloy and produces effects on the mechanical properties which have not been thoroughly investigated. The experiments of Lange and Ichewsky tend to show that, with steels, there is an increase of ductility and tenacity. According to Arnold, the ultimate strength of pearlitic steels bears a definite relation to the state of separation of the eutectoid constituents. It appears that coalescence lessens the effect of any later heat treatment, more particularly quenching.

D. *Crystalline Equilibrium.*—This effect applies particularly to cold-worked materials which undergo recrystallisation on annealing in the manner previously described (see p. 71). Annealing, which tends to increase the grain size, will, if prolonged, or carried out at too high a temperature, produce a very weak structure consisting of large crystal grains.

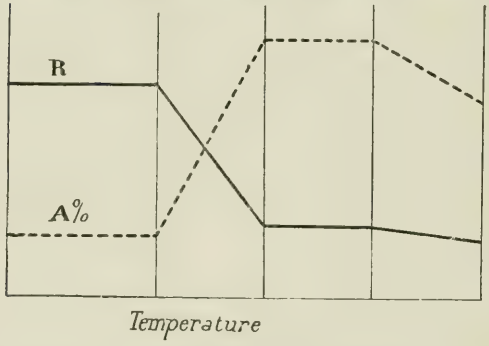


FIG. 204.—Diagrammatic annealing curves for cold-worked material.

Many recent researches undertaken on this important subject of annealing have shown the effects of increasing temperatures. Four distinct ranges may be found with all materials examined:—

1st Temperature Range: effect nil; the material retains its initial values.

2nd Temperature Range: the effect gradually increases; the properties vary with the temperature; the ultimate strength, the elastic limit and the hardness diminish, whilst the percentage elongation, percentage reduction in area, and the impact figures increase.

3rd Temperature Range: constant effect; the properties retain the values they had at the upper limit of the second temperature range. The material is now completely annealed.

4th Temperature Range: negative effect; all the mechanical properties diminish in value simultaneously, ultimate stress, percentage elongation, impact figures, all decrease; the material has been overheated.

Fig. 204 illustrates diagrammatically the four temperature ranges. The temperatures defining the commencement and end of the respective temperature ranges are dependent on the compositions of the alloy. Several diagrams are given (Figs. 205–208) in illustration of the effects of cold-work and annealing.

HE EFFECT OF COLD WORK ON THE STRUCTURE OF ANNEALED COPPER

(GRARD.)

Etchant: Ferric chloride.

(× 85.)

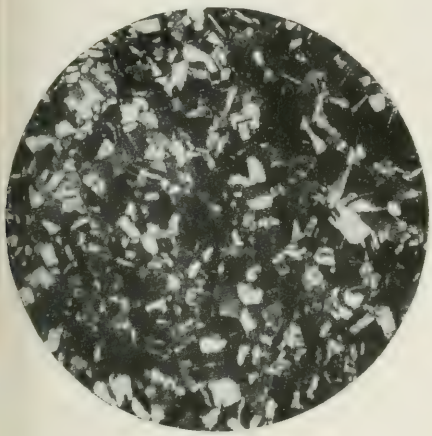


FIG. 148.—Annealed copper.

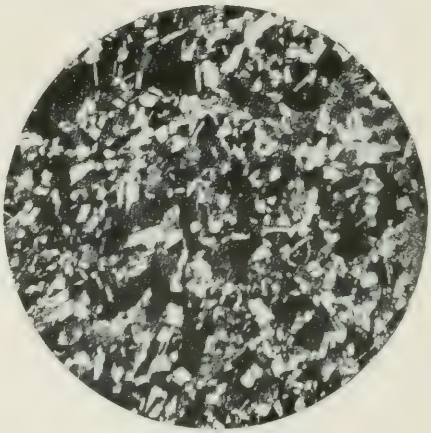


FIG. 149. 5 % reduction.

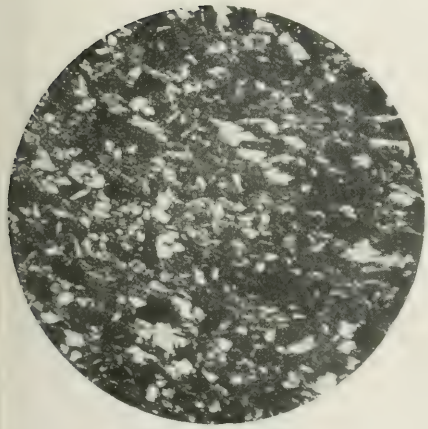


FIG. 150.—10 % reduction.

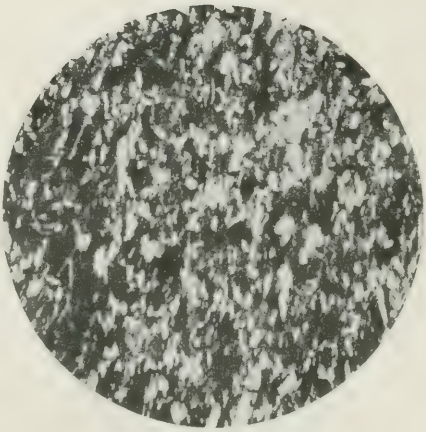


FIG. 151.—20 % reduction.

EFFECT OF COLD WORK ON COPPER (*cont.*).

(GRARD.)

Etchant : Ferric chloride.
(× 85.)

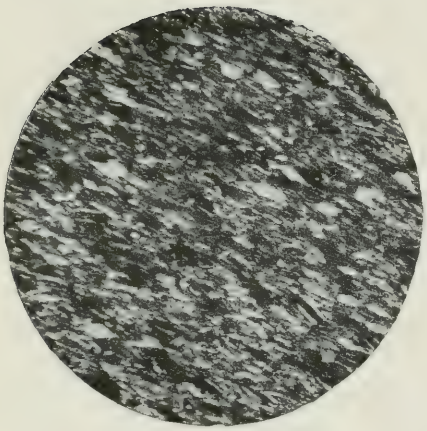


FIG. 152.—50 % reduction.

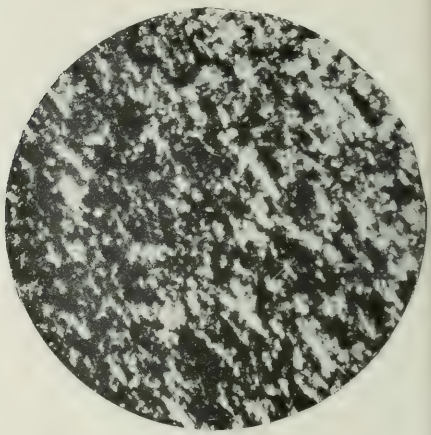


FIG. 153.—100 % reduction.

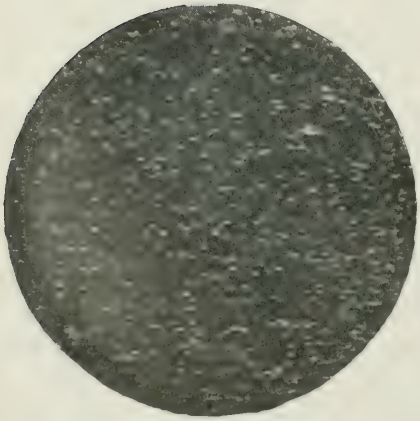


FIG. 154.—300 % reduction.

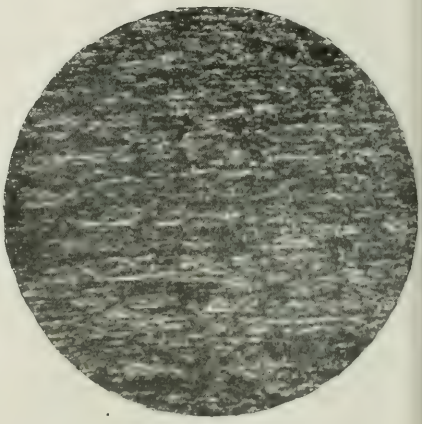


FIG. 155.—600 % reduction.

EFFECT OF ANNEALING COLD-WORKED COPPER.

(GRARD.)

Etchant; Ferric chloride.
(× 85.)

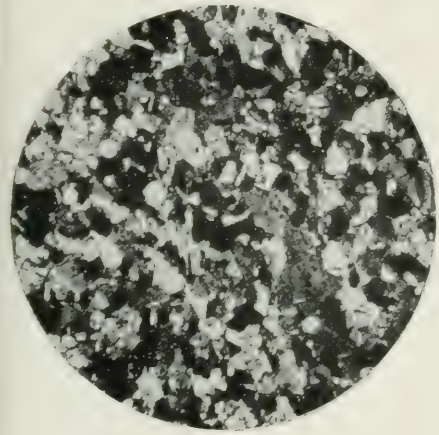


FIG. 156.—Ordinary copper plate.

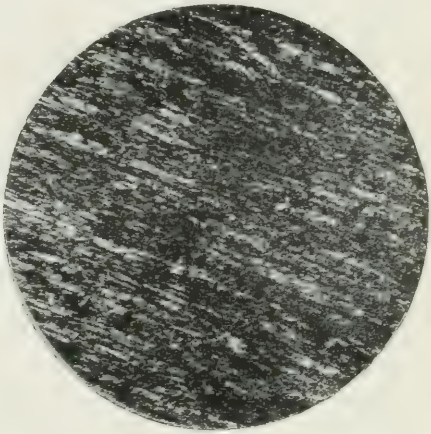


FIG. 157.—Cold worked copper.

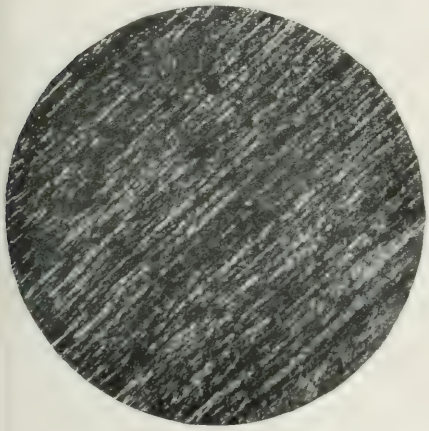


FIG. 158.—Copper annealed at 100° C.

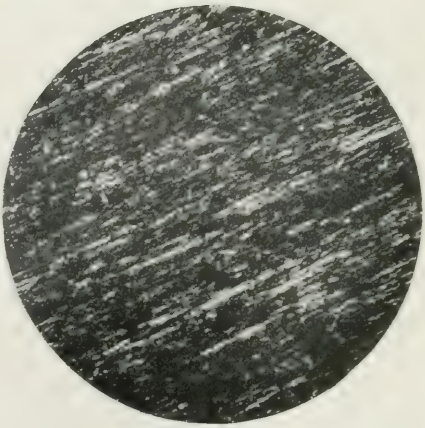


FIG. 159.—Copper annealed at 150° C.

EFFECT OF ANNEALING COLD-WORKED COPPER (*cont.*).

(GRARD.)

Etchant : Ferric chloride.

(× 85.)

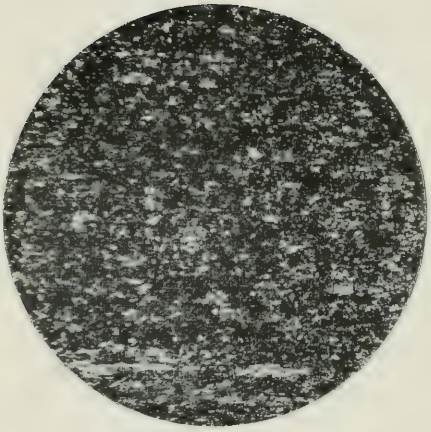


FIG. 160.—Copper annealed at 175° C.

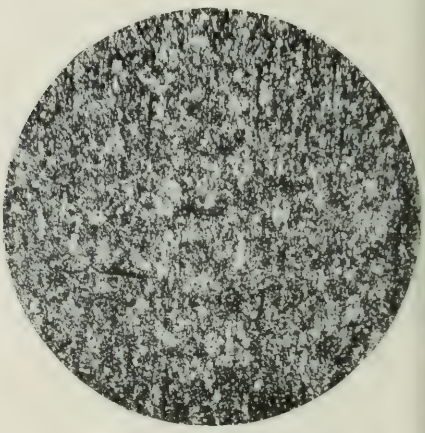


FIG. 161.—Copper annealed at 200° C.

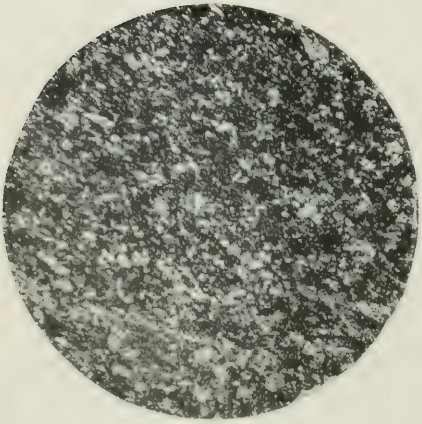


FIG. 162.—Copper annealed at 250° C.

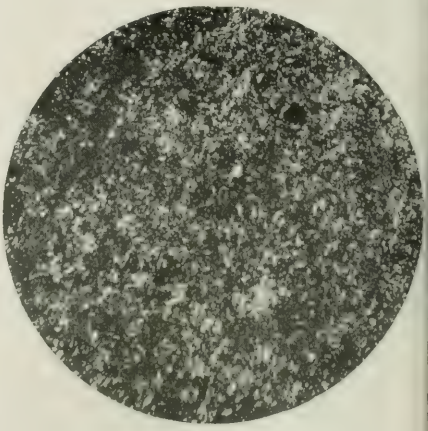


FIG 163.—Copper annealed at 300° C.

EFFECT OF ANNEALING COLD-WORKED COPPER (*cont.*).

(GRARD.)

Etchant: Ferric chloride.

(× 85.)

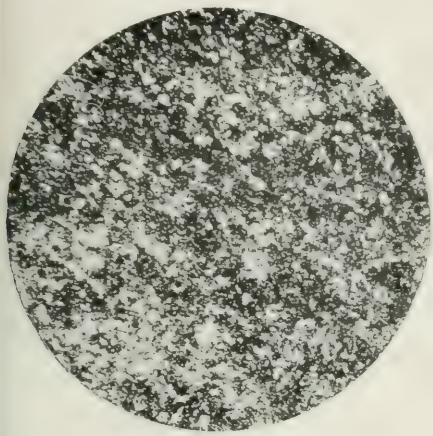


FIG. 164.—Copper annealed at 400° C.

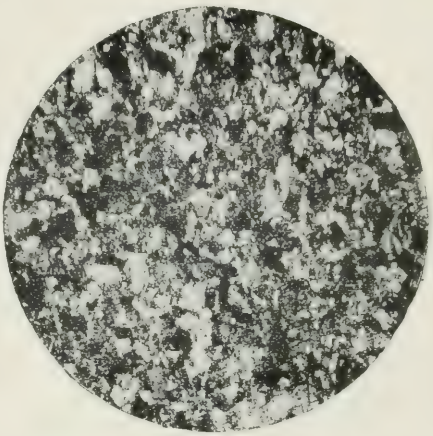


FIG. 165.—Copper annealed at 500° C.

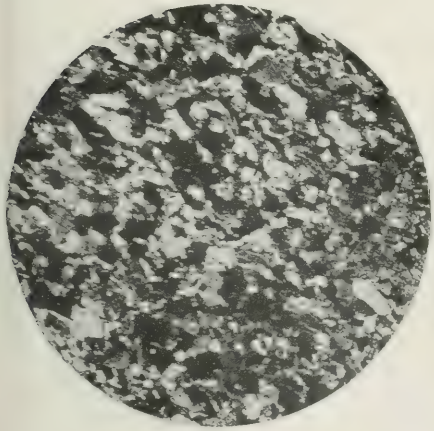


FIG. 166.—Copper annealed at 600° C.

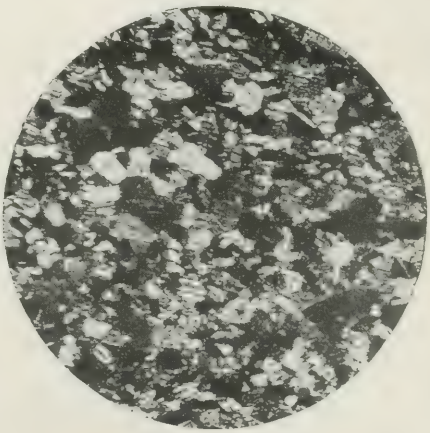


FIG. 167.—Copper annealed at 700° C.

EFFECT OF ANNEALING COLD-WORKED COPPER (*cont.*).

(GRARD.)

Etchant : Ferric chloride.

(× 85.)

FIG. 168.—Copper annealed at 800° C.

FIG. 169.—Copper annealed at 900° C.

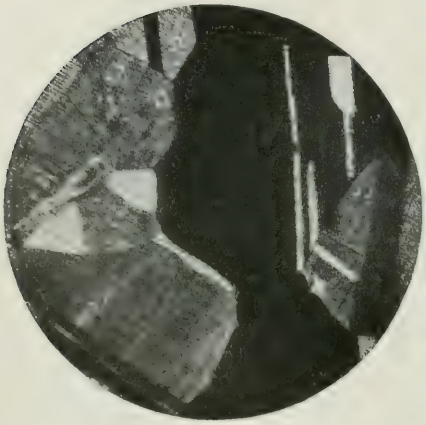


FIG. 170.—Copper annealed at 950° C.

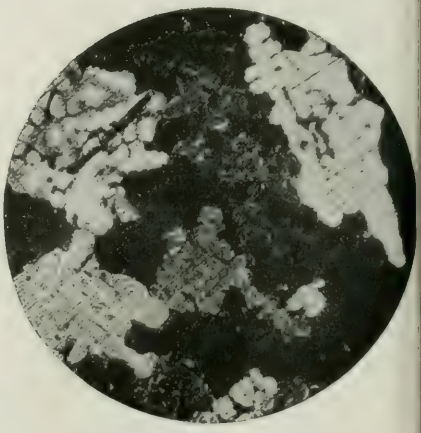


FIG. 171.—Copper melted.

EFFECT OF COLD-WORK ON BRASS.

Cu = 67 ; Zn = 33.

(GRARD.)

Etchant : Ferric chloride.

(× 85.)

FIG. 172.—Annealed brass, 67 Cu ; 33 Zn.

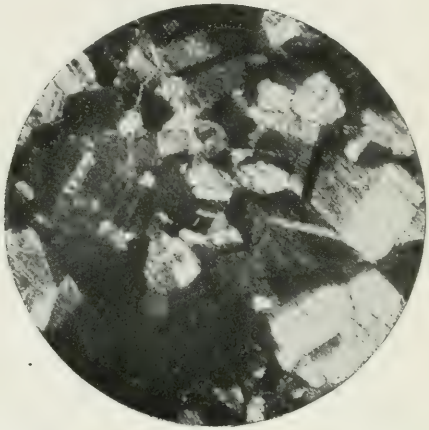


FIG. 173.—5 % reduction.

FIG. 174.—10 % reduction.

FIG. 175.—15 % reduction.

EFFECT OF COLD-WORK ON BRASS (*cont.*).

Cu = 67 ; Zn = 33.

(GRARD.)

Etchant : Ferric chloride.

(× 85.)

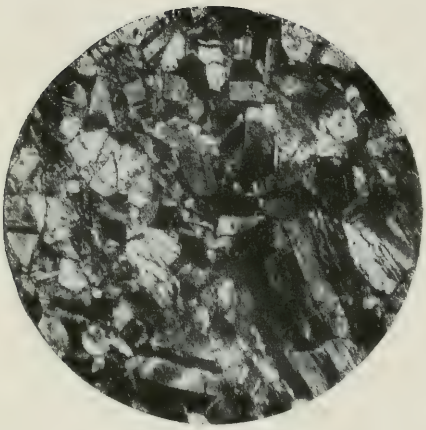


FIG. 176.—20 % reduction.

FIG. 177.—25 % reduction.

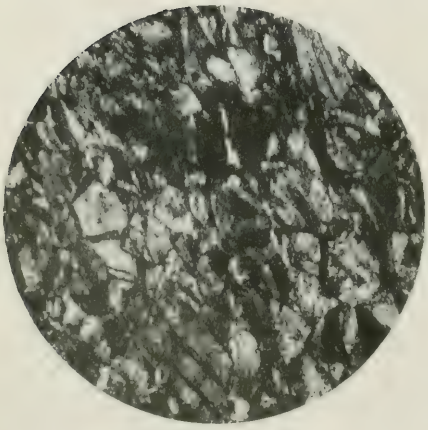


FIG. 178. 35 % reduction.

FIG. 179.—50 % reduction.

EFFECT OF COLD-WORK ON BRASS (*cont.*).

Cu = 67 ; Zn = 33.

(GRARD.)

Etchant : Ferric chloride.

(× 85.)

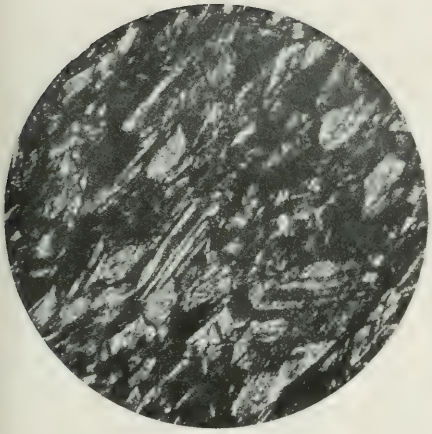


FIG. 180.—80 % reduction.

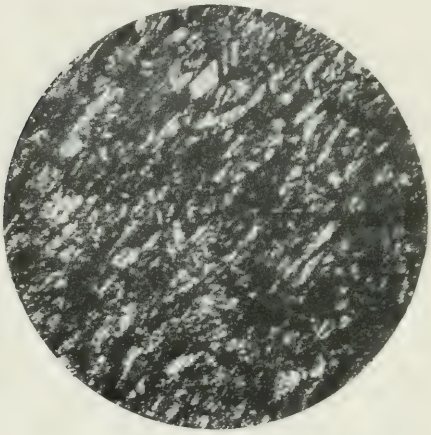


FIG. 181.—100 % reduction.

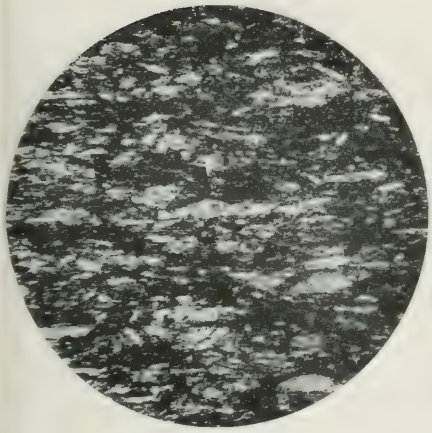


FIG. 182.—125 % reduction.

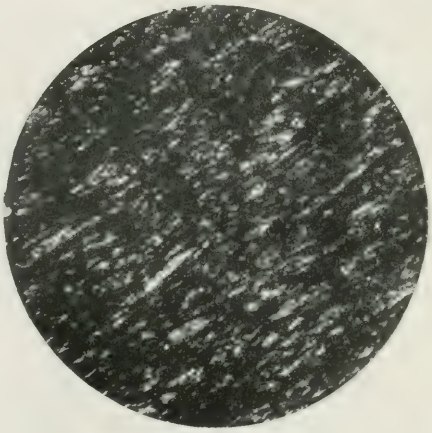


FIG 183.—150 % reduction.

EFFECT OF COLD-WORK ON BRASS (*cont.*).

Cu = 67 ; Zn = 33.

(GRARD.)

Etchant : Ferric chloride.

(× 85.)

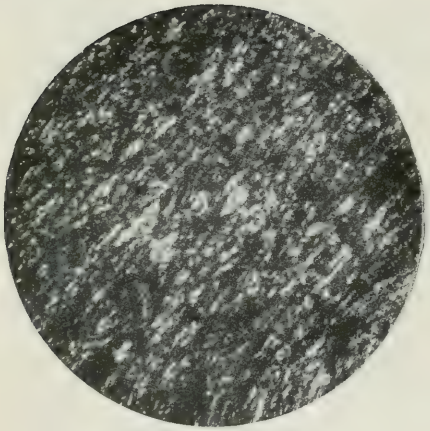


FIG. 184.—200 % reduction.

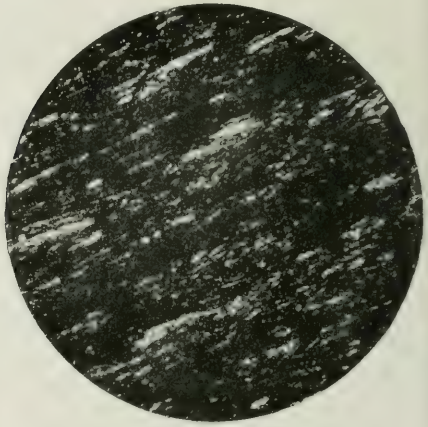


FIG. 185.—250 % reduction.

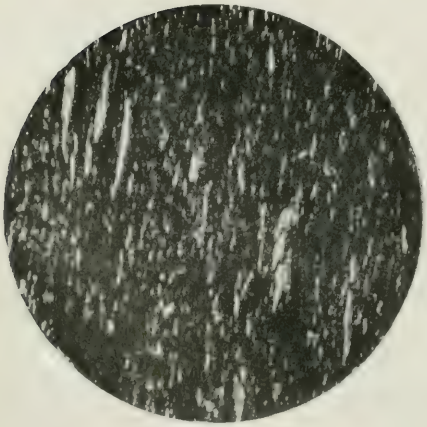


FIG. 186.—350 % reduction.

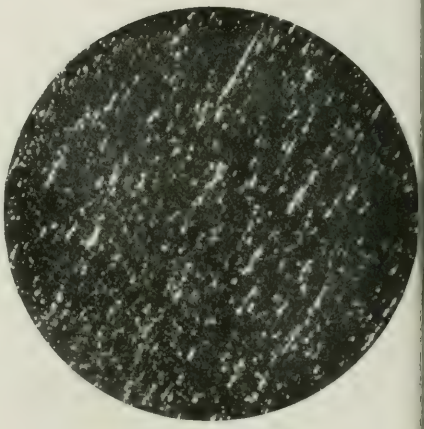


FIG. 187 —600 % reduction.

EFFECT OF ANNEALING BRASS.

Cu = 67 ; Zn = 33 cold rolled.
(GRARD.)

Etchant : Ferric chloride.
(× 85.)

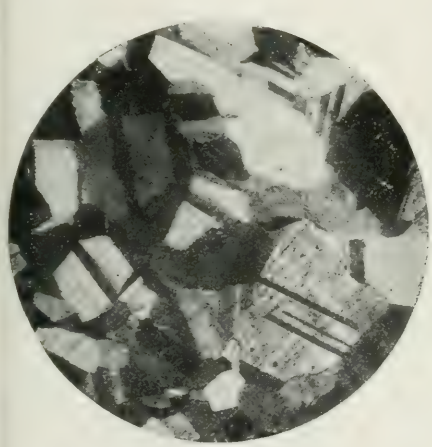


FIG. 188.—Ordinary brass plate.

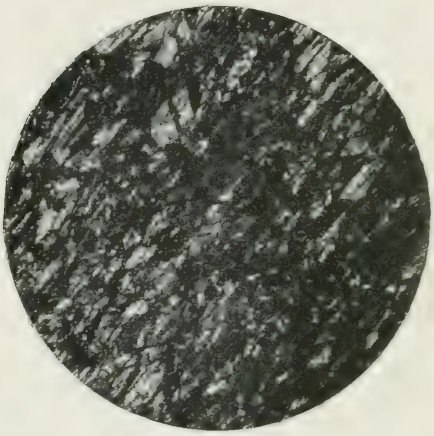


FIG. 189.—Cold rolled.

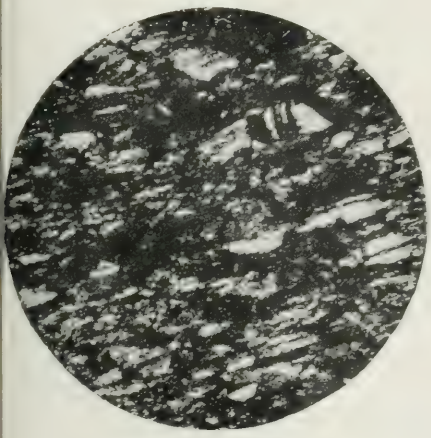


FIG. 190.—Annealed at 200° C.

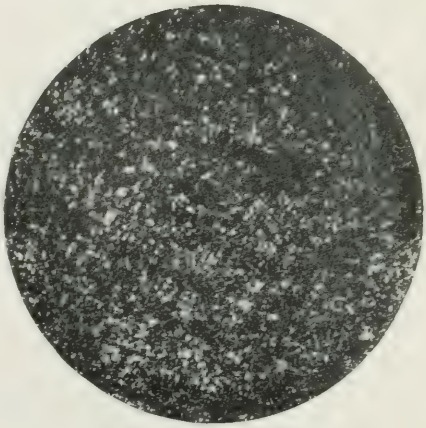


FIG. 191.—Annealed at 300° C.

EFFECT OF ANNEALING BRASS (*cont.*).

Cu = 67 ; Zn = 33 cold rolled.

(GRARD.)

Etchant : Ferric chloride.

(× 85.)

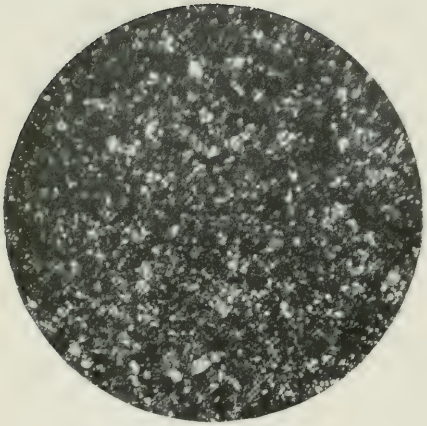


FIG. 192.—Annealed at 350° C.

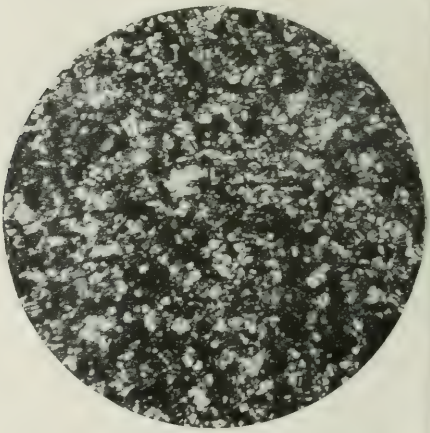


FIG. 193.—Annealed at 400° C.

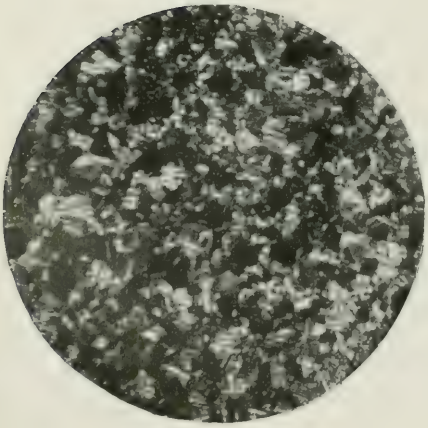


FIG. 194.—Annealed at 450° C.

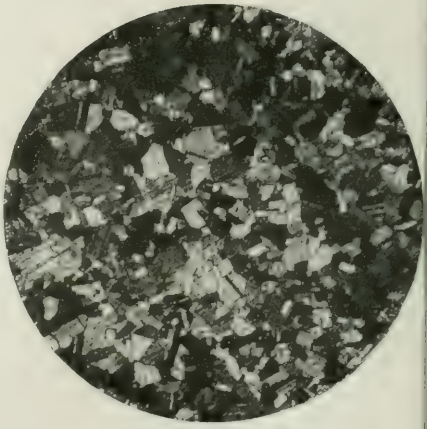


FIG. 195.—Annealed at 500° C.

EFFECT OF ANNEALING BRASS (*cont.*).

Cu = 67 ; Zn = 33 cold rolled.

(GRARD.)

Etchant : Ferric chloride.

(× 85.)

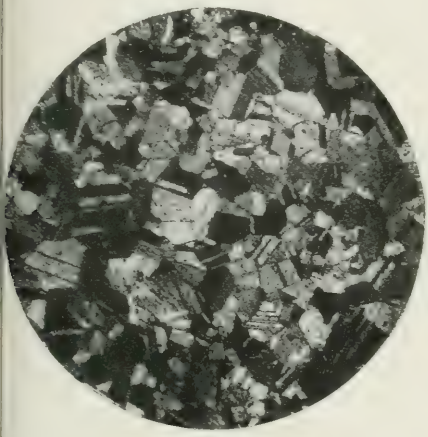


FIG. 196.—Annealed at 550° C.

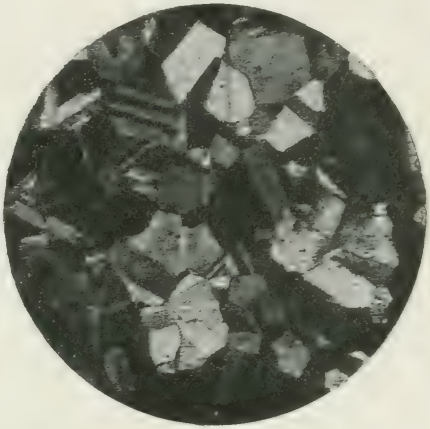


FIG. 197.—Annealed at 600° C.

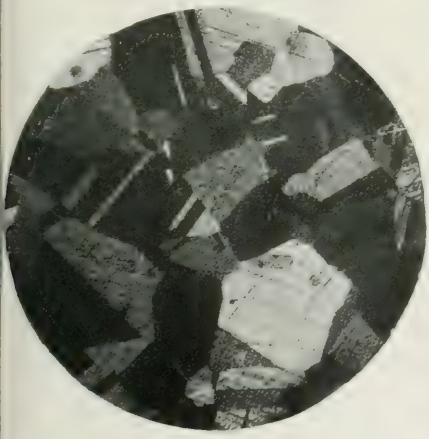


FIG. 198.—Annealed at 650° C.

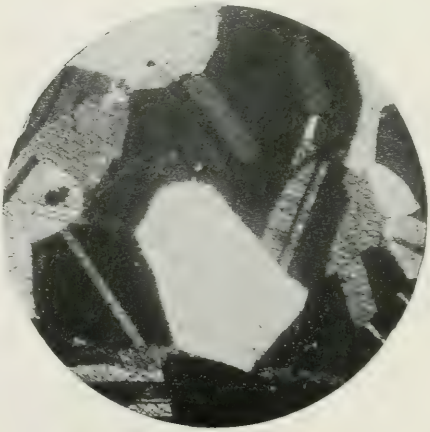


FIG. 199.—Annealed at 700° C.

EFFECT OF ANNEALING BRASS (*cont.*).

Cu = 67 ; Zn = 33.

(GRARD.)

Etchant: Ferric chloride.

(× 85.)

FIG. 200.—Brass, annealed at 750° C.

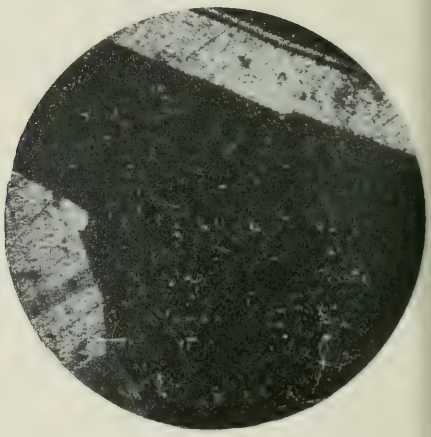


FIG. 201.—Brass, annealed at 800° C.

FIG. 202.—Brass, annealed at 850° C.

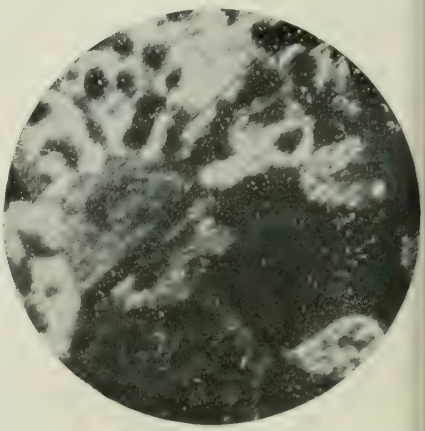


FIG. 203.—Brass, annealed at 900° C.

The following examples are due to Grard (*Revue de Metallurgie*, "Mémoires," iv. 1069, 1909). The experiments were performed on

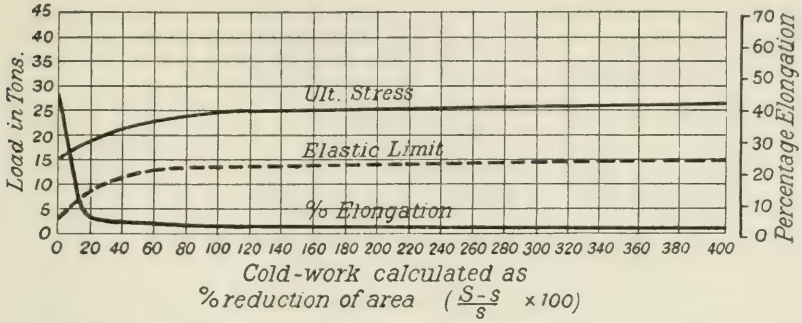


FIG. 205.—Variations in the mechanical properties of copper as a function of the work-hardness (Grard).

pure copper and brass containing 67 per cent. copper and 33 per cent. zinc—French cartridge-case brass.

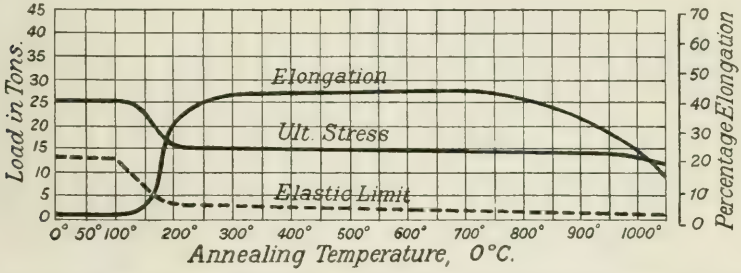


FIG. 206.—Effect of annealing on the properties of cold-worked copper (Grard).

The different temperature ranges are very clearly indicated in these instances, and the variations in the annealing temperatures for

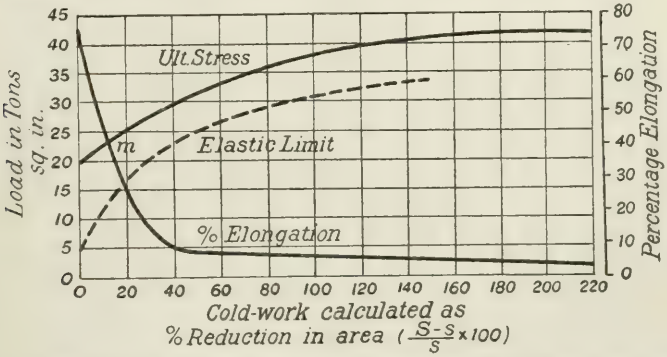


FIG. 207.—Variations in the mechanical properties of cold-worked cartridge brass (Cu 67, Zn 33) (Grard).

different metals will be observed. Cold-worked copper, particularly, shows a distinct change at a temperature of approximately 150° C., when recrystallisation commences.

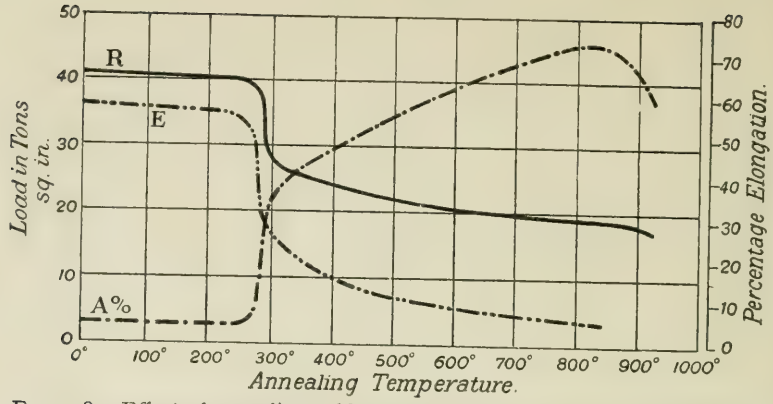


FIG. 208.—Effect of annealing cold-worked brass (Cu=67, Zn=33) (Grard).

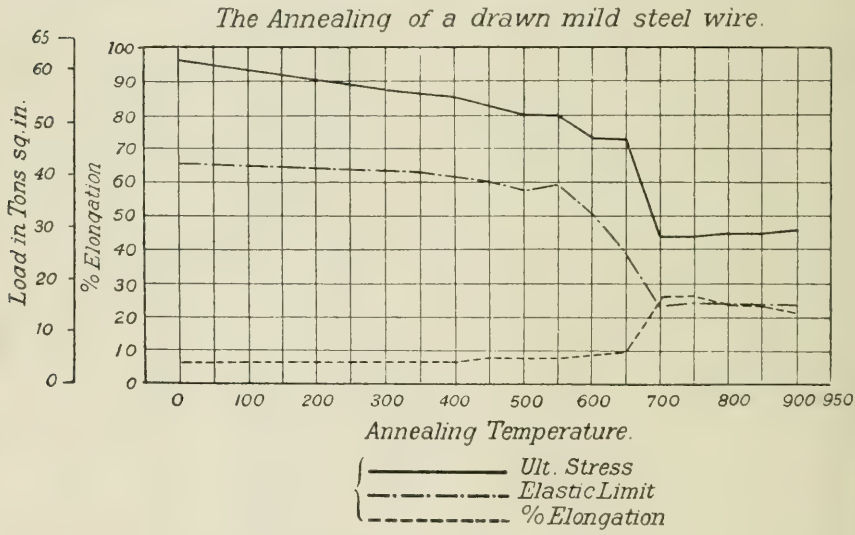


FIG. 209.

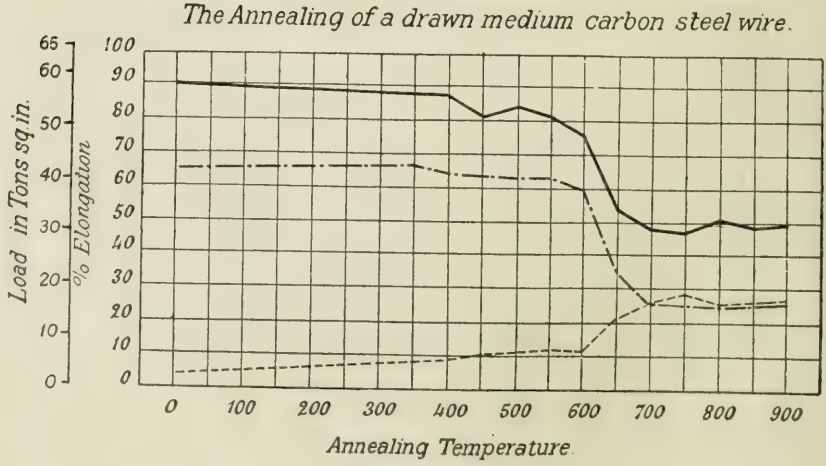


FIG. 210.

The micrographs illustrated in Plates XIX. to XXXII. (Figs. 148–203, see p. 120) should be examined in conjunction with the curves given in Figs. 205–208.

Figs. 209–211 show the effect of annealing cold-drawn steel and nickel wires.[1]

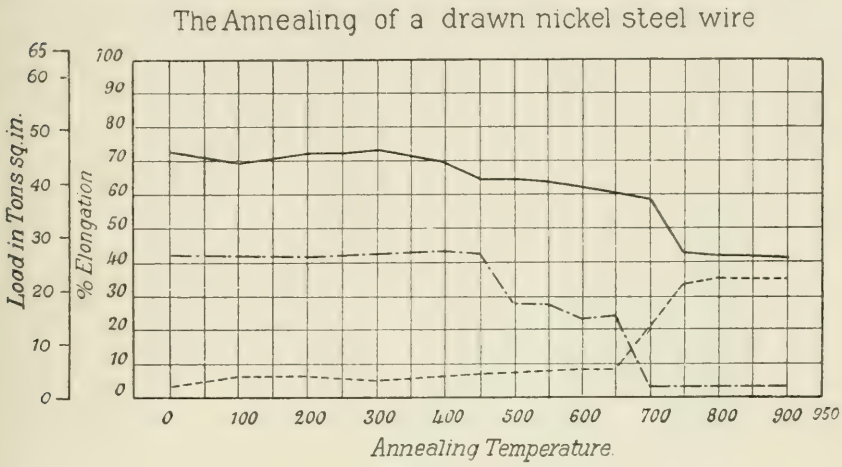


FIG. 211.

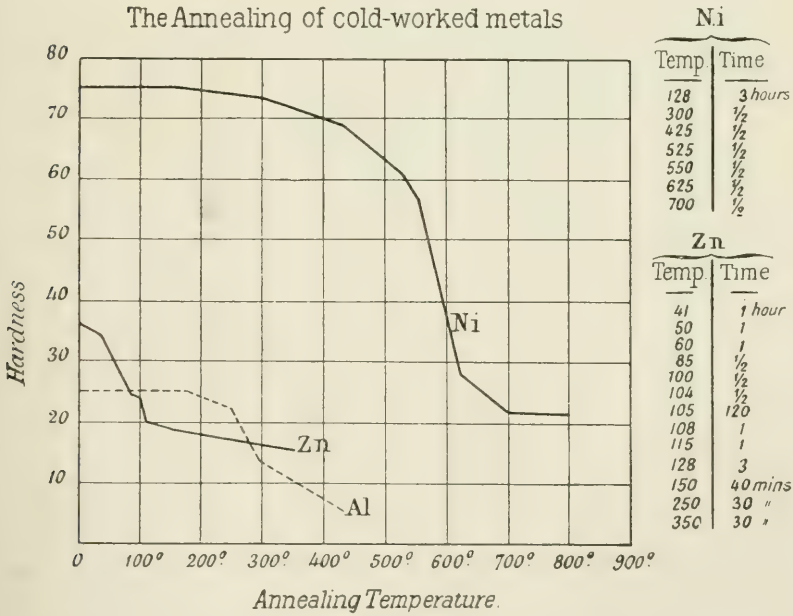


FIG. 212.

Finally, Figs. 212–213 give the scleroscope hardness figures obtained by Kirke Rose on various cold-worked materials after varying periods of annealing.[2]

[1] Guillet, *Revue de Met.*, "Mémoires," p. 665, 1913.
[2] *Proc. Inst. of Metals*, pp. 1–31, 1912.

The Effect of Annealing when the Material passes through a Transformation Point on Heating.—Assume, in the first instance, that the transformation occurs without any hysteresis effect (retardation effect), annealing will exert an influence on the distribution of the constituents and on their individual structure.

Effect on the distribution of the constituents: this explains the transformation of Widmanstaetten's acicular structure to cellular structure (see p. 76), and the consequent improvement in the mechanical properties produced by annealing; the material becomes less brittle.

Effect on the individual structure of the constituents: the

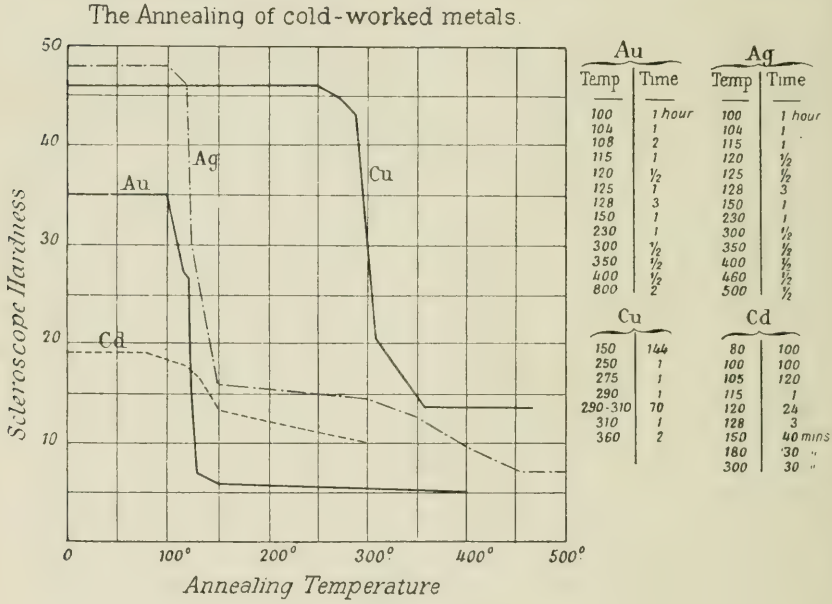


Fig. 213.

effect is similar to that of an indirect polymorphic transformation (p. 73), giving rise to an increase in the number of crystal grains.[1] This action occurs in annealing any overheated material; the brittleness is decreased, the coarse structure destroyed, and the material is said to have been *refined*. Thus only alloys possessing intermediate transformation points are capable of being refined by heat treatment alone, without the intervention of mechanical treatment.

The case of an alloy having a pronounced hysteresis effect will now be considered. In this case the transformation temperature is lowered considerably, even at comparatively slow rates of cooling. The result of annealing at a temperature above the transformation

[1] Example, transformation of β to γ iron.

temperature on heating is to produce a form of quenching effect. The only method to soften the metal in this case is to give a prolonged annealing at a temperature as near to the transformation temperature as possible, but not above this temperature. Certain nickel and chrome steels may be quoted as examples of this type of metal. One of the authors has shown that, by a special treatment followed by very slow cooling, this material will be in such a condition that any subsequent industrial annealing will be equivalent to quenching.[1]

Tempering.—Tempering consists in annealing a quenched material at a temperature below its transformation temperature.

Tempering removes the internal strains, causes the work hardness produced by quenching to disappear, and tends to re-establish equilibrium conditions.

The extent of its effect will depend on the temperature and the time the material is heated. Recent research has shown the time of heating to be an important factor.[2] Thus, the higher the temperature and the longer the time of heating, the greater the tempering effect produced.[3]

It should be observed that tempering a quenched specimen in which any of the stable component at high temperatures is present will, in the first instance, increase the hardness.[4] An example of this type will be found in the description dealing with the tempering of steels.

Chemical Treatment

Metals and alloys are subjected to numerous chemical treatments, and metallography has proved of great assistance in controlling and examining the effects of such treatment. Many examples are quoted in the later chapters, but in the present instance only a few typical cases are selected.

Microscopical examination will show :—

1. If the desired reaction has taken place.
2. The effect of such a reaction.
3. In many cases, the quality of the result.

The cementation of steel and the manufacture of malleable castings are typical examples, and are considered in the next chapter.

Again, in tinning, galvanising, nickel-plating, and other dipping

[1] Portevin, Proc. Inter. Assoc. for testing materials, French and Belgian members, 1911.

[2] Guillet and Portevin, *Rev. de Met.*, vi. 102, 1909.

[3] Brant has shown that the electrical resistance of quenched steels, measured by Barus in 1885, had decreased 20 per cent. in the interval of twenty-four years. Shottky has found a sensible evolution of heat at 100° C., and Brush and Hadfield have described changes that have occurred in quenched steels at ordinary temperatures.

[4] Portevin, *C. R.*, 158, 1174, April, 1914. Portevin et Arnou, *C. R.*, 154, 511, 1912.

and electro-plating operations, it is possible to examine and find the thickness of the deposit and also, and this is equally important, whether an intermediate alloy has been formed between the case and the metal treated. This intermediate alloy, which does not always exist, greatly improves the adherent properties of the deposit (Pl. XXXIII., Fig. 215, p. 136). Metallographic examination is also of assistance in determining the qualities of soldered, brazed, and welded joints ; it is possible to determine the quality of such joints by the examination of the structure of the surrounding metal (overheating), and by the formation of intermediate alloys in cases where another alloy is employed to make the joint. It can be easily seen whether the two parts are merely stuck together, which is frequently the case in practice. An example is shown, Pl. XXXIII., Fig. 214 (p. 136) ; the solder is seen to exist as a separate alloy between the two pieces of aluminium.

CHAPTER IV

INDUSTRIAL APPLICATION OF METALLOGRAPHY TO STEELS AND CAST IRONS

IRON ALLOYS—DEFINITIONS

STEEL and cast iron are essentially iron-carbon alloys, but they always contain small quantities of other elements derived from the raw materials from which they are produced: manganese, sulphur, silicon, phosphorus, in solid solution as impurities; isolated particles of various materials: oxides, sulphides, phosphides, silicates, which are also impurities, but are termed *inclusions* (the term *sonims* has also been suggested for the non-metallic impurities present in steel). The term *cast iron* is confined to iron-carbon alloys which contain sufficient carbon to render them non-malleable at all temperatures; commercial cast irons contain between 2·5 and 4 per cent. carbon. Special steels and cast irons are produced when elements, other than those they usually contain, are added to ordinary steels and cast irons (such as nickel, chromium, tungsten, vanadium, molybdenum), or when the amounts of certain impurities (such as manganese, silicon) are intentionally increased in order to improve certain properties of the material. These steels are also termed alloy steels. The special elements (chromium, tungsten, vanadium, silicon, manganese) are usually added to the molten metal in the form of iron alloys rich in these metals and also containing varying amounts of carbon; these alloys are termed *ferro-alloys*. Therefore, if the impurities and inclusions are disregarded, iron and steel alloys may be classified as follows:—

1. Ordinary steels and cast irons are alloys of iron and carbon, hence the term carbon steels.

The ordinary carbon steels are classified commercially as follows:

	Carbon content (per cent.).	Mechanical tests of annealed metal.		
		Ult. stress (tons sq. in.).	Elastic limit.	Percentage elongation.
Very mild steel ..	0·05–0·15	20–24	12–15	34–28
Mild steel ..	0·15–0·25	24–30	15–18	28–25
Low carbon steel ..	0·25–0·40	30–35	18–20	25–22
Medium ,, ,, ..	0·40–0·60	35–40	20–24	22–18
Hard steels	0·60–0·70	40–47	24–28	18–14
or	0·70–0·80	47–54	28–32	14–8
High carbon steels	0·80	54–65	32–35	8–5

2. The special steels and cast irons are alloys of Fe+C+M, and are known as ferro-alloys when the content of the special metals (M) is very high.

The ternary steels will consist of Fe—C—M.

The quarternary steels will consist of Fe—C—M—N, and so forth.

1. ORDINARY CARBON STEELS AND CAST IRONS

Equilibrium Diagrams.[1]—The iron carbon alloys are characterised by the existence of two possible equilibrium conditions which are not equally stable; the first corresponds to the presence of graphite, the other to that of cementite or iron carbide, Fe_3C; this is illustrated by two diagrams which can be partially superimposed.

1. Stable equilibrium diagram (Fig. 216).
2. Labile or metastable equilibrium diagram (Fig. 217).

The two diagrams are shown superimposed in Fig 218. In accordance with the previous description it will be observed that the lines of the stable equilibrium diagram are situated above the corresponding lines of the other diagram.

Although the industrial iron-carbon alloys, with the exception of grey cast irons, conform to the labile equilibrium system both diagrams have been described. The sections of each diagram will be considered in the following order commencing with the stable diagram: solidification; liquidus and solidus; transformation points.

(*a*) *Stable Equilibrium Diagram: Graphite* (Figs. 216–218).—The liquidus consists of the two branches AB and BD; AB corresponds to the separation of a solid solution or "mixed crystal" of iron and carbon from the liquid, the carbon content varying from 0 to 1·4 per cent. C (point *a*); BD marks the separation of graphite, and is the solubility curve for graphite in the liquid metal; AB and BD meet at the eutectic point B; at this point, the liquid, containing 4·3 per cent. C, completely solidifies as a eutectic of graphite and 1·4 per cent. C, solid solution.

The solidus consists of A*a* and the eutectic horizontal *a*C. The line A*a* which had been traced hypothetically by Roozeboom, has been determined experimentally by Roberts Austen, and again by Carpenter and Keeling, by means of cooling curves, by Saldaou by the electrical resistance method, and by Gutowski, Wark, Goerens, Meyer, and Saldaou by the microscopical examination of quenched alloys.

[1] Recent researches, notably those by Wittorf, have explored the alloys of high carbon content and have completed the diagram, but with slight modifications; the area investigated is outside the limits of commercial alloys.

After solidification there exists: below A*a* and in the vicinity of that line, an homogeneous solid solution if the rate of cooling has been sufficiently slow; below *a*B, solid solution surrounded by eutectic; below BC, flakes of graphite surrounded by eutectic. Considered accord-

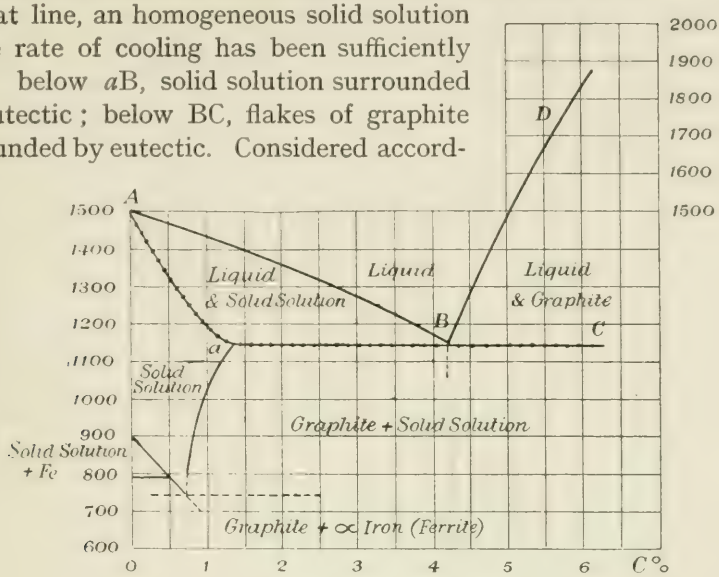
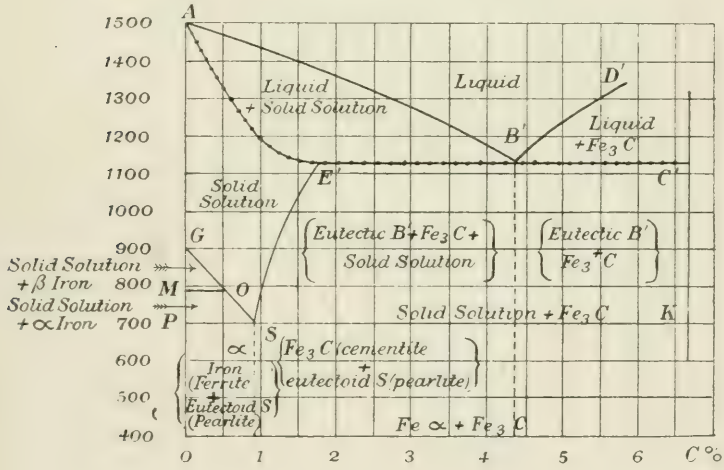


FIG. 216.—Stable equilibrium diagram.



G	=	917°		
O	=	769°	&	0.48 % C
S	=	725°	"	0.9 % "
E	=	1.130°	"	1.7 % "
B'	=	1.130°	"	4.3 % "
A	=	1.150°	"	

FIG. 217.—Labile equilibrium diagram.

ing to the phase rule, there exist: a solid solution and a mixture of solid solution+graphite.

The cooling curves show transformations occurring in the completely solid state; besides the two phases, solid solution and

graphite, a third phase ferrite or pure iron separates from the solid solution Fe—C; equilibrium then exists between the solid solution and ferrite, and also between the solid solution and graphite.

The equilibrium curves for solid solution-ferrite are the same for both stable and labile equilibriums (Figs. 216–217); their outline corresponds exactly with the classic work of Osmond. The data obtained from these researches showed that, up to 0·9 per cent. C, pure iron, separates from the solid solution at varying temperatures, the iron thus separated existing as two allotropic modifications α and β; in the case of pure iron the transformation from α to β occurs at 769° C

α iron is magnetic, β is non-magnetic, neither form is capable of dissolving carbon. Therefore the iron in the solid solution exists as a third allotropic modification, γ

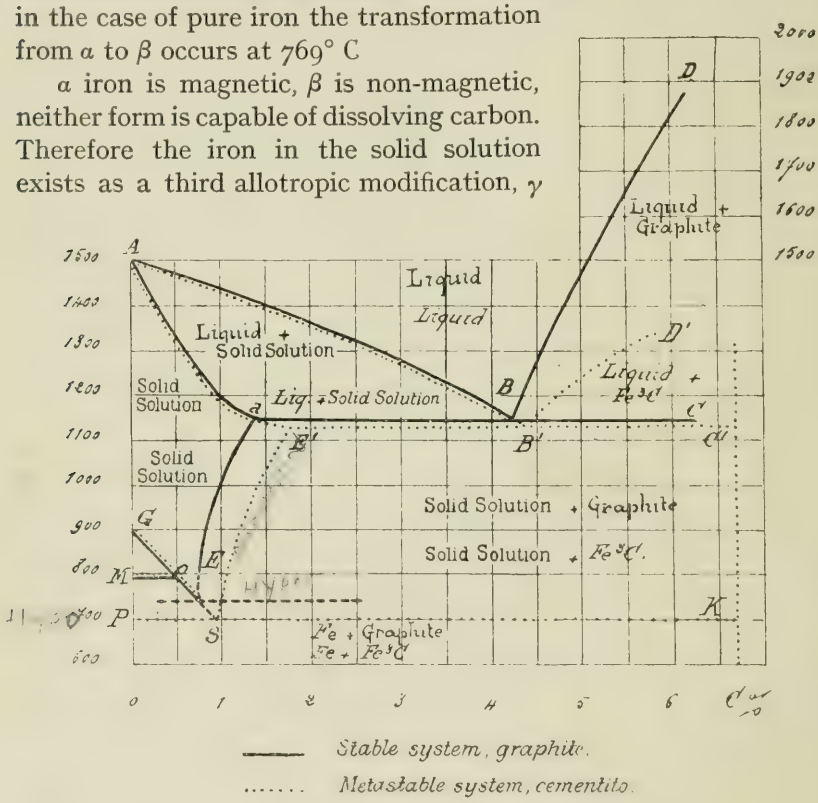


FIG. 218.

iron, which, like β, is non-magnetic. The curve showing the separation of iron from the solid solution is also the transformation curve of γ to β or α iron. This curve consists of two branches: GO corresponding to the liberation of β iron, OS corresponding to the liberation of α iron; the equilibrium of the three phases, α iron, β iron, and solid solution, indicates a transition point corresponding to the horizontal MO at 769° C.

However, the existence of β iron indicated, according to Osmond, by thermal analysis and modifications in the magnetic properties, is now not admitted by many authorities, more particularly since

the formulation of the magnetic theories (Weiss). Since its existence is not of importance in the treatment and microscopical examination of the iron carbon alloys, it will be neglected in the present instance, and the horizontal MO will be disregarded. It will therefore be considered that α iron separates from the solid solution (γ iron-carbon) along the line GOS. The extent of this line GOS is limited by its intersection with the curve *a*E (equilibrium solid solution-graphite). This curve, commencing from a point *a*, has been drawn according to the figures obtained by Charpy, Ruer, and Iljin. Its junction with the line GOS gives a point which should correspond to a eutectoid ferrite-graphite which has not been observed. Specimens have been obtained that contained spots impossible to polish, and for this reason have been considered as graphite; these spots may consist of an intimate mixture of graphite and ferrite, rendered indistinct by the former. In any case, these spots never occupy the whole surface, and even when the carbon content is considerably in excess of the eutectoid composition ferrite is still present in quantity. If equilibrium conditions were completely attained, only two phases, ferrite and graphite, would finally exist; this never occurs, except in the case of certain grey cast irons, and then there is always some cementite present, corresponding to the labile equilibrium conditions.

(*b*) *Diagram of Labile Equilibrium* (*Cementite*) (Figs. 217–218).—If surfusion of the graphite occurs in the liquid alloy, owing to more rapid cooling or the presence of certain foreign elements (Mn, Cr), the line BD is suppressed and, instead of graphite, cementite separates from the liquid along a line B′D′, corresponding to the equilibrium between liquid-cementite.

The liquidus consists of the lines AB′ and B′D′ which cut one another at the point B′; separation of the solid solution continues until the point B′ is reached, when solidification is completed at this point (B′) by the formation of a eutectic: solid solution-cementite.

The solidus is formed by the lines AE′ and E′B′C′. The points E′ and B′ are defined by the intersection of the line A*a* and the extension of AB with the eutectic horizontal E′C′. This occurs, according to the results obtained by Charpy and Grenet, at 1130° C., the difference between the eutectic temperatures of the two systems being 20° C. The point E′ corresponds to 1·70 per cent. C.

The two phases cementite and solid solution exist after solidification; during cooling and in alloys containing 0–0·9 per cent. C, α iron or ferrite is liberated from the solid solution, as previously described, along the line GOS. The junction of the lines GOS (defining the separation of the ferrite) and SE′ (defining the separation of cementite from the solid solution) at the point S mark the formation, at 723° C., of the eutectoid pearlite containing 0·9 per cent. carbon.

The curve E′S (separation of cementite from solid solution) has been plotted according to the cooling curves obtained by Osmond, Roberts Austen, Carpenter and Keeling, and Wark. Goerens and Saldaou have made similar determinations by the microscopical examination of quenched specimens ; Tchijersky and Choulgine by etching in vacuo at high temperatures ; Saldaou by measurement of the change in electrical resistance. The curve is practically a straight line).

Phases present.—Below the line PSK only two phases exist, α iron or ferrite, and the definite compound cementite, Fe_3C, which corresponds to the vertical C′K.

If the distribution of the individual particles of these two phases is considered, it is possible to make further distinctions as regards the constitution of iron carbon alloys in the metastable condition at ordinary temperatures owing to the existence of the eutectic B and the eutectoid S : between 0 and 0·9 per cent. C (below GOS) the alloys consist of ferrite which has separated along GOS and the eutectoid S ; this eutectoid of ferrite and cementite generally presents an extremely fine structure consisting of alternate lamellæ of the two constituents which are only visible under the highest magnifications ; it has received the name *pearlite* and its mean carbon content is 0·9 per cent. C. The steels containing less than 0·9 per cent. C are known as hypoeutectoid steels, sometimes incorrectly termed hypo-eutectic steels, and consist of pearlite and ferrite ; the ferrite that has separated before the formation of the eutectoid pearlite is occasionally termed *pro-eutectoid* or *extra-eutectoid ferrite* to distinguish it from the ferrite contained in the pearlite or "*pearlitic*" *ferrite.*

Between 0·9 and 1·7 per cent. C (below SE′), the alloys will consist of cementite that has separated along SE′ and pearlite formed on passing the horizontal PSK, as in the previous case ; these steels are termed hypereutectoid steels (incorrectly hypereutectic steels), and contain cementite that has separated from the solid solution before the formation of the eutectoid—*pro-eutectoid cementite,* and the eutectoid, *pearlite.*

The cementite intermixed with the pearlitic ferrite to form the eutectoid is termed *pearlitic cementite.*

Compositions between 1·7 and 4·3 per cent. C (below the section E′B′ of the horizontal E′B′C′). During solidification the solid solution separates along AB′ and solidification is completed by the formation of the eutectic B′ (cementite-solid solution). From this solid solution which, at the temperature E′B′C′ (1130° C.), contains 1·7 per cent. C (point E), cementite separates out along E′S until the solid solution contains 0·9 per cent. C, and is converted into the eutectoid pearlite on crossing the horizontal PSK.

Finally, there will exist.

(*a*) *Eutectic cementite*, the cementite occurring as a constituent of the eutectic B′.

(*b*) *Pro-eutectoid cementite*, the cementite separating along SE′, as described above.

(*c*) *Pearlite* formed at 723° C., consisting of alternate lamellæ of eutectoid cementite and eutectoid ferrite.

Compositions between 4·3 per cent. C and 6·6 per cent. C (below the horizontal B′C′). During solidification cementite separates along B′D′ and solidification is completed by the formation of the eutectic B′ (cementite-solid solution containing 1·7 per cent. C). This solid solution undergoes transformations on cooling as indicated above.

Finally, there will exist :

(*a*) *Primary cementite*, separated from the liquid along B′D′.

(*b*) *Eutectic cementite*, formed at the temperature B′C′ (1130° C.).

(*c*) *Pro-eutectoid cementite*, that has separated along SE′.

(*d*) *Pearlite*, formed at 723° C. and consisting of alternate lamellæ of eutectoid cementite and eutectoid ferrite.

The varying character and distribution of the constituents, ferrite, cementite, pearlite, due to their method of formation, will be described later. Fig. 295, Pl. LIII. (*see* p. 152), shows the complete series of iron carbon alloys in the metastable state.

Conditions of Formation and Transition of the Stable and Labile Equilibrium Conditions.—Stable equilibrium conditions occur more readily, the greater the carbon content and the higher the temperature ; some elements, even in small quantities, such as silicon and aluminium, act as catalysers and facilitate the formation of graphite. Apart from the effect of these foreign elements, it may be stated that *in practice* graphite will only occur in slowly cooled or annealed cast irons, or those high in silicon or other foreign elements that act as catalysers. Inversely the metastable conditions and the presence of cementite (diagram, Fig. 217) will be observed :

1. In all steels cooled and annealed in an ordinary manner.

2. In rapidly cooled cast irons (chill cast), those containing very little silicon and aluminium, and also those containing such foreign elements as manganese, chromium, etc., which facilitate the formation of the labile constituents and hinder the formation of graphite.

Graphite may be produced :

1. During the period of solidification.

2. During cooling after solidification.

3. By annealing white cast iron (temper carbon).

Thus, by annealing, graphite may be liberated from cementite according to the reaction,

$$Fe_3C \rightarrow Fe + C$$

which reaction is irreversible within the range of temperature employed for industrial annealing. The reaction only occurs at comparatively high temperatures and is more pronounced the higher the temperature (interference effect decreases). Inversely, it is impossible for carbon, present in an alloy in the graphitic condition, to combine with the iron to form cementite unless it passes into liquid or solid solution. The graphite must either be dissolved by the liquid metal or else taken into solid solution, when this is possible, after which cementite may be obtained by rapid cooling. Owing to the relative slowness of the reaction $Fe_3C \rightarrow Fe_3+C$, alloys are frequently found to exist in a state intermediate between the stable and metastable conditions, the first being indicated by the presence of graphite and ferrite, the second by one or both of the constituents, cementite and pearlite.

It will be observed that, owing to the existence of two sets of equilibrium conditions, three phases may exist at ordinary temperatures: Fe, Fe_3C, and C (graphite), forming four constituents, three of which correspond to the preceding phases: ferrite, cementite, and graphite, and the fourth, a eutectoid mixture of the first two phases or pearlite.

Transformations occurring in the Iron-Carbon Alloys.—The only transformation occurring in iron-carbon alloys containing above 1·7 per cent. C, is defined by the eutectoid line PK which extends from 0 to 6·6 per cent. C.

As previously mentioned, in the case of the alloys containing less than 1·7 per cent. C it is only necessary to consider the metastable condition; the equilibrium transformation temperatures will therefore be given by Fig. 217. It will be observed that, according to the carbon content, a steel may show one, two, or three transformation points corresponding to the lines GOS, MO, SE′, and PK (Fig. 217).

Pure Iron.—The allotropic modifications of iron are indicated by two transformation points corresponding to the points G and M on the diagram.

It is usual to refer to these transformations as A_3 and A_2, A_3 corresponding to the higher transformation temperature and A_2 to the rapid change in the magnetic properties.

2. **Steels containing less than 0·3 per cent. C.**—There are three transformation points shown by the lines GO, MO, and PS. A_3 indicates the commencement of the segregation of iron in the solid solution (γ iron-carbon); this point is depressed as the carbon content increases and eventually coincides with the point A_2, the position of which is independent of the carbon content.

The point A_1 corresponds, on cooling, to the formation of the eutectoid pearlite, the quantity of which increases with the carbon

content up to the point S; the liberation of heat increases in a corresponding manner.

3. **Steels containing between 0·3 per cent. and 0·9 per cent. C.**—These have two transformation points: The $A_{3,2}$ point, corresponding to the line OS, is depressed as the carbon content increases and indicates the separation of α iron from the solid solution (γ iron-carbon); the second is the point A_1 which remains constant at the eutectoid temperature. With 0·9 per cent. C (point S), the point $A_{3,2,1}$ alone exists.

4. **Steels containing between 0·9 per cent. and 1·7 per cent. C.**—Two transformation points exist: the first corresponds to the separation of cementite from the solid solution along SE′; it rises rapidly with the carbon content and is termed the A_{cm} point; the second $A_{3,2,1}$ is the equilibrium temperature of the three phases; solid solution containing 0·9 per cent. C, ferrite, and cementite; the temperature of this point remains constant (line SK).

5. **Alloys containing above 1·7 per cent. C.**—The transformation point $A_{3,2,1}$ alone exists, and is shown by the line SK.

As a general rule the point A_3 is clearly indicated by arrests in the cooling curves and by the dilatation and electrical resistance methods.

The point A_2 may be identified by thermal analysis, but more definitely by the magnetic method.

The point A_1 is very clearly indicated by the usual methods of thermal analysis and by dilatation; it is not well defined by the electrical resistance method.

Effect of Heat Treatment—Transitional Constituents and Constituents not in Equilibrium.—The effects produced by annealing and varying rates of cooling on cast irons and other alloys of sufficiently high carbon content, have been considered as regards the stability of the equilibrium conditions, indicated by the presence of graphite or cementite.

The effects produced on the various transformation points, the equilibrium temperatures for which are given by the diagram, still remain to be considered. These transformations are of primary importance, especially in the case of steels.

The transformations only occur at the same temperature on heating and cooling, when the rates of heating and cooling are exceptionally slow; as a general rule, for a definite transformation A, a transformation temperature A_c, above A, will be found on heating and a transformation temperature A_r, below A, will be found on cooling.

Supercooling frequently occurs at the point Ar_1, producing a recalescence effect; the rise in temperature is such that with steels

containing 0·9 per cent. C it may amount to 100° C, and may be observed with the naked eye if the metal is examined in a subdued light. Because of the effects produced by undercooling and variations in the transformation times, it is possible, by suitably controlling the rate of cooling, to lower the transformation temperatures on cooling and thereby obtain, by suitable quenching, definite structures not in equilibrium (Chap. II.).

With steels the transformation on cooling occurs normally in two stages :

1. Separation of pro-eutectoid ferrite or cementite along the line GOS or SE′.

2. Formation of the eutectoid pearlite at the temperature PSK.

By varying the quenching temperature and rate of cooling it is possible to modify either both or only the second transformation, the second transformation having the greater effect on the mechanical properties.

Consider, as an example, a steel containing 0·9 per cent. C, presenting a single transformation temperature on cooling, $Ar_{3\cdot2\cdot1}$ corresponding to the reaction :

$$\text{solid solution } (\gamma \text{ iron} + \text{C}) \rightarrow \frac{\text{ferrite} + \text{cementite}}{\text{pearlite}}$$

the complete retention of the solid solution (impossible in practice) at ordinary temperatures by the complete suppression of the transformation would give *austenite*, a non-magnetic homogeneous constituent consisting of the solid solution (γ iron—C) ; inversely, the transformation completely effected at approximately the equilibrium temperature would give the constituent *pearlite*, a eutectoid aggregate of ferrite and cementite.

Between these two constituents, the one not in physico-chemical equilibrium (austenite), the other in physico-chemical equilibrium (pearlite), there exists a series of varying conditions possessing definite appearance and structure. The principal structures are considered as transitional constituents and have received the names *martensite, troostite, osmondite, sorbite.*

These constituents will be considered in the order obtained by quenching under conditions of decreasing quenching effect : this classification therefore represents the passage from austenite to pearlite. None of these constituents is in structural equilibrium ; sorbite, osmondite and troostite are in physico-chemical equilibrium ; martensite, in all probability, is not in physico-chemical equilibrium. Inversely, the following modifications occur on annealing the quenched alloys :

austenite → martensite → troostite → osmondite → sorbite → lamellar pearlite

each constituent being converted to the next in rotation. In certain

FIG. 214.—Solder joint, showing the solder as a separate alloy between the two sheets of aluminium.

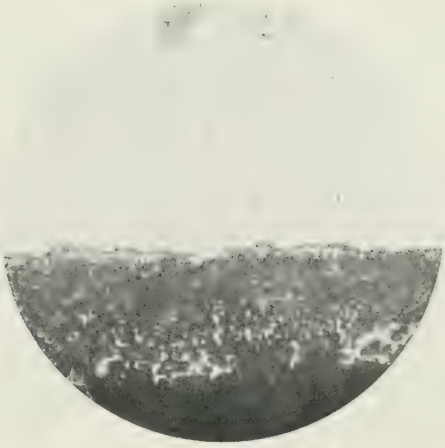
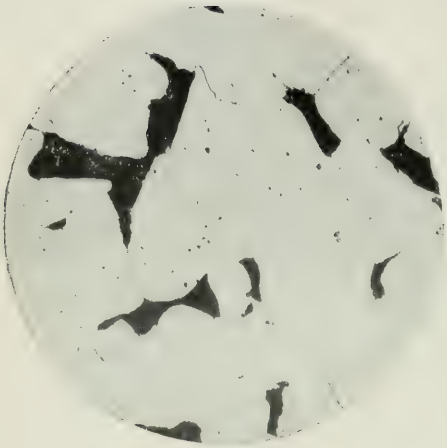


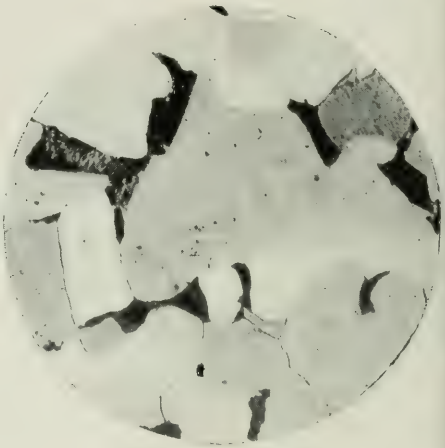
FIG. 215.—Galvanised iron, showing the formation of a special constituent (white) in a black background.

CONSTITUENTS OF ANNEALED CARBON STEELS.

(× 200.)

Ferrite and pearlite in a mild steel.





FIGS. 219–220.—Etchant: Kourbatoff's Reagent.

Ordinary etching: Dark pearlite, light ferrite, with dark lines outlining crystal boundaries.

Deep etching: The ferrite crystals are differentially discoloured.

Slag inclusions, ferrite, pearlite and cementite, in puddled steel.

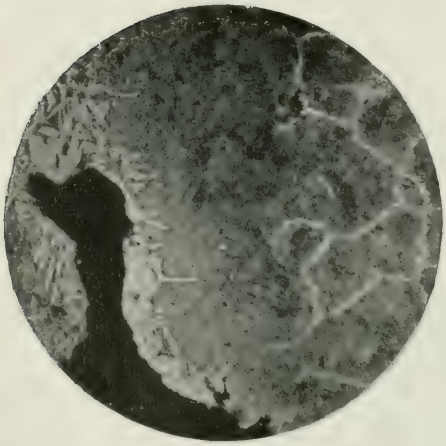


FIG. 221.—Etchant: Picric acid. Slag, black (visible unetched); pearlite, shaded portion; ferrite and cementite, white.

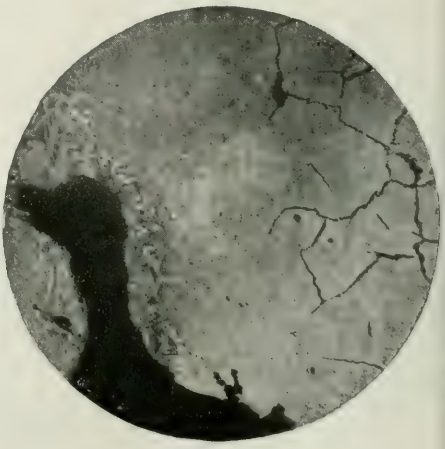
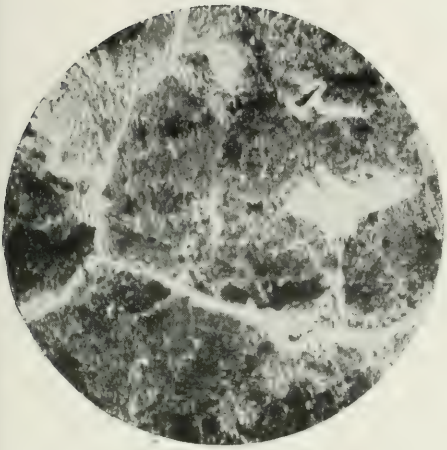


FIG. 222.—Same field etched with sod. picrate. Slag, black (visible unetched); very dark lines of cementite; lighter ground mass of pearlite; white ferrite.

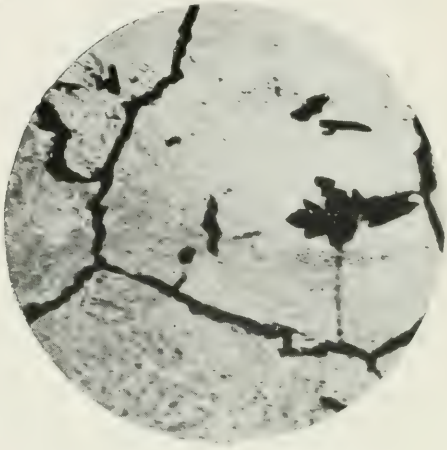
CONSTITUENTS OF ANNEALED CARBON STEELS.

(× 200.)

Cementite and pearlite in hypereutectoid steel.

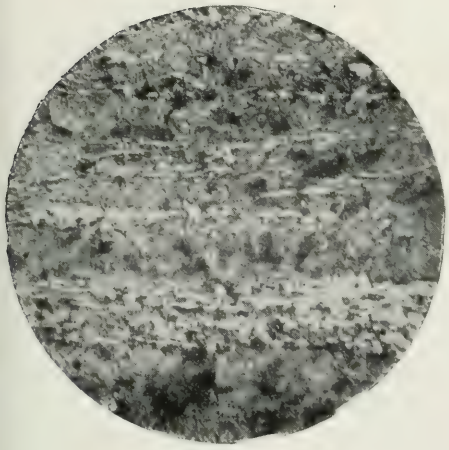


Etchant: Picric acid. White cementite; dark pearlite.

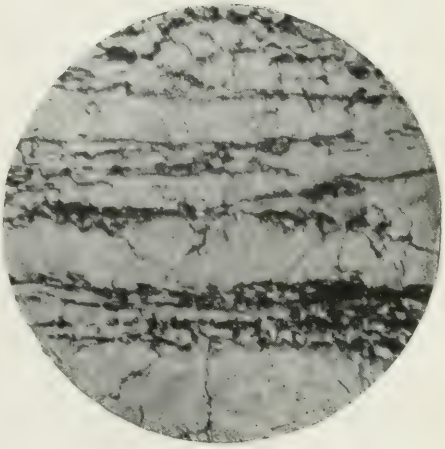


The same field etched with sod. picrate. Dark cementite; light pearlite.

FIGS. 223–224.—Section at right angles to direction of rolling (transverse section); cementite network.



Etchant: As above.



Etchant: As above.

FIGS. 225–226.—Section in the direction of rolling (longitudinal section); banded cementite.

CONSTITUENTS OF ANNEALED CARBON STEELS.

FIGS. 227–228.—**Pure pearlite in slowly cooled steel.**

Etchant: picric acid.

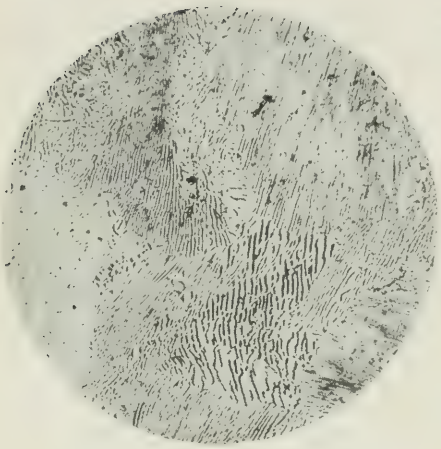


FIG. 227.
(× 200.)

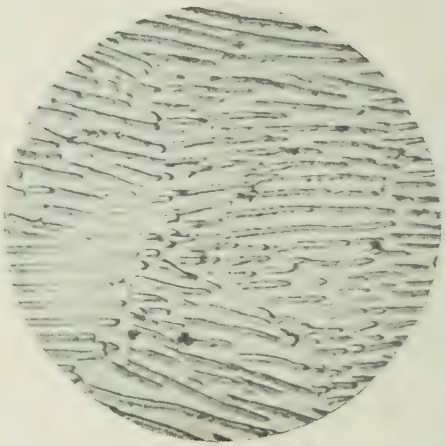


FIG. 228.
(× 1200.)

FIGS. 229–230.—**Cementite and pearlite.**

Etchant: Picric acid. Light cementite; dark pearlite.

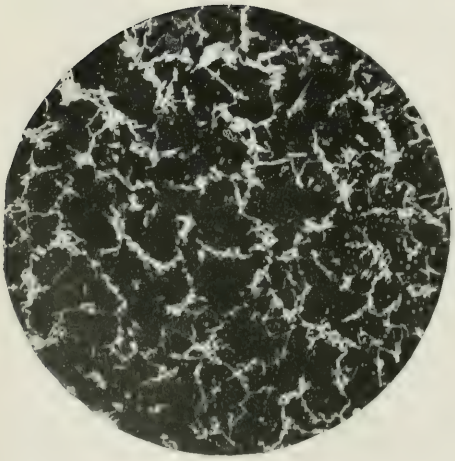


FIG. 229.—Rolled steel, 2·2 % C.
Transverse section.

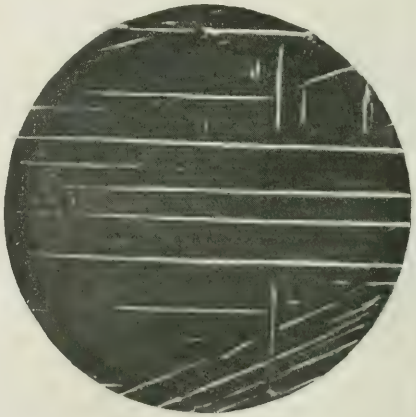


FIG. 230.—Cementite needles in a cemented steel.

cases, one or more of the stages may not appear, thus the annealing of austenite may give rise to the direct formation of troostite. In the cases of hypereutectoid and hypoeutectoid steels, the alloy may be retained, at least partially, in the condition stable at high temperatures; thus alloys are obtained containing unchanged austenite of variable carbon content. The formation of this austenite is dependent on the quenching temperature, the speed of quenching or cooling, and the carbon content (in the case of special steels, certain elements such as Mn and Ni accelerate the formation of austenite by lowering the transformation temperature and increasing the interference ("passive resistance") effect. It is necessary to combine the effects of these three factors to obtain the maximum amount of austenite; Osmond obtained this combined effect by quenching small specimens containing 1·66 per cent. C from a temperature above 1000° C. in iced water.

A reduction of one of these three factors tends to bring about the formation of martensite or one of the other transitional constituents, but it must not be overlooked that since the transformation in these cases occurs in two stages, it is possible to obtain a mixture of these constituents (transitional) together with the pro-eutectoid ferrite or cementite by varying the quenching temperature and rate of cooling. The constituents of the iron-carbon series may now be summarised as follows:

Constituents in equilibrium: ferrite, cementite, pearlite, graphite.

Constituents not in equilibrium: austenite.

Transitional constituents: martensite, troostite, osmondite, sorbite.

These various constituents may now be considered in detail.

Ferrite

Definition.—Free alpha iron; may contain small quantities of certain impurities (Si, P, Mn, . . .) in solid solution.

Properties.—Cubic system. Compared with the other constituents it is soft and of low tensile strength (20 tons sq. in.), very ductile, strongly magnetic, coercive force very small. Hardness, Mohs' scale, 3·5–3·7 (Behrens).

Etching.—The usual reagents (picric acid, Bénédick's reagent) do not discolour this constituent but merely reveal the crystal boundaries as dark lines (Fig. 51, Pl. III., p. 68; Fig. 219, Pl. XXXIV.; Fig. 254, Pl. XLIII., p. 144). Deeper or more prolonged etching reveals the different orientation of the grains (Fig. 220, Pl. XXXIV.), and finally produces etching figures on the surface of the specimen; this result is more readily obtained by using Heyn's solution (12 per cent. copper-ammonium chloride followed by 10 per

cent. nitric acid) (*see* Fig. 53, Pl. III., p. 68). It should be observed that the presence of impurities facilitates the differential coloration of the crystal grains.

Structure.—1. Ferrite may exist in annealed steels as—

(*a*) As a pro-eutectoid constituent existing with the pearlite; in this case it appears as irregular grains intermixed with the pearlite (Figs. 219–220, Pl. XXXIV., p. 136), as a network outlining the pearlite areas (cellular structure: Fig. 90, Pl. XI., p. 144), as plates of varying orientation (Widmanstaetten structure: Figs. 92–93, Pl. XI., p. 144; Fig. 278, Pl. XLIX., p. 144); combinations of these various types will also be observed.

(*b*) As a constituent of the eutectoid pearlite occurring as lamellæ separated by the lamellæ of cementite.

(*c*) Co-existing with the cementite in cases where the pearlite eutectoid structure has been destroyed by coalescence.

2. In annealed white irons (or even in hard steels that have been subjected to abnormal conditions of annealing or cooling, and in special steels containing silicon, aluminium, or vanadium) as a result of the decomposition—

$$\underset{\text{Cementite.}}{Fe_3C} \rightarrow \underset{\text{Ferrite.}}{3\,Fe} + \underset{\text{Graphite.}}{C}$$

In this case, where there is decomposition of the primary cementite, the ferrite surrounds the graphite that is produced (Fig. 379, Pl. LXXI, and Fig. 384, Pl. LXXII.).

3. In quenched or quenched and annealed hypoeutectoid steels, intermixed with the martensite or other transitional constituent as irregular jagged plates or fine needles.

In certain instances the distribution of the ferrite appears to be greatly affected by the presence of impurities and inclusions (Figs. 250 and 252, Pl. XLII., p. 144), and presents the characteristic banded appearance known as *ghost lines*.

It has been shown that etching reveals the outline of the crystal grains and etching figures. The size of these grains depends partly on the heat treatment and partly on the presence of various impurities.

Phosphorus and silicon increase the size of the crystal grains, whilst nickel and chromium tend to produce a finer grain structure. In certain special instances, it is possible to distinguish Neumann's lines, mechanical cleavages produced by shock or forging at too low a temperature.[1]

Cementite

Definition.—Carbide of iron Fe_3C corresponding to 6·7 per cent. carbon by weight.

Properties.—Orthorhombic system. Hardest constituent of steel

[1] Ref. Osmond and Cartaud, *Revue de Met.*, vol. iii., p. 668, 1906; Portevin and Durand, *Revue de Met.*, vol. xi., p. 771, 1914.

(hardness=6 Mohs' scale, scratches glass, does not scratch quartz).[1] Very brittle. Specific magnetism about two-thirds that of pure iron.

Etching.—It is only attacked by boiling sodium picrate [2] (Figs. 224 and 226, Pl. XXXV., p. 137) and oxidising etching in air, and is thus easily distinguished from all other constituents of steel with the sole exception of iron phosphide. When polished it stands in relief in the softer material, and this characteristic may be verified by examining the shadows produced when a specimen is viewed by oblique illumination ; it is not attacked by any of the usual etching reagents.

Structure.—1. Cementite may exist—

(*a*) As primary cementite (alloys containing above 4·3 per cent. C) in the form of plates or thin layers in white cast irons (Figs. 301–303, Pl. XV., p. 89).

(*b*) As eutectic cementite (alloys containing above 1·7 per cent. C) appearing as a network enclosing the products of decomposition of the solid solution (1·7 per cent. C) during cooling. With normal cooling the solid solution splits up into pearlite and pro-eutectoid cementite (Fig. 294, Pl. LIII. ; Figs. 296–297. Pl. LIV., p. 152).

(*c*) As pro-eutectoid cementite (alloys containing above 0·9 per cent. C) separating, between the eutectic and eutectoid temperatures, from the solid solution of gamma iron and carbon ; therefore two main methods of separation are possible : cellular appearance as a network between the original crystal grains of the solid solution (Fig. 91, Pl. XI., p. 73 ; Figs. 221–222, Pl. XXXIV., p. 137 ; Fig. 229, Pl. XXXVI., p. 137) ; as fine plates or needles (Fig. 230, Pl. XXXVI.), or as needles commencing from the network and projecting into the interior of the grains along the cleavage planes.[3]

The method of formation is dependent on the cooling conditions. Mechanical deformation and rolling will obviously affect the regularity of these structures (Figs. 225–226, Pl. XXXV., p. 137). If there is any of the cementite-solid solution eutectic present (alloys containing above 4·3 per cent. C) the pro-eutectoid cementite will tend to be deposited along the edges of the eutectic areas in the form of a border.

(*d*) Pearlitic cementite as lamellæ forming one constituent of the eutectoid pearlite.

(*e*) Spheroidised cementite : as small rounded grains in granular pearlite, formed by the coalescence of pearlitic cementite (Fig. 91,

[1] According to Ruff and Gersten the hardness is much lower (3·2–3·3 Mohs' scale).

[2] When the thickness of the cementite plates is less than 0·001 mm., sodium picrate has no etching effect ; therefore fine pearlite remains unattacked (Le Chatelier).

[3] Refer to Howe and Levy, " la biographie de la cémentite pro-eutectoide " (*Rev. de Met.*, vol. ix., p. 1075, 1912).

Pl. XII., p. 78; Figs. 270–773, Pl. XLVII., p. 144); as irregular plates in the ferrite, this structure being found, more particularly, in steels that have been subjected to prolonged annealing, which permits the pearlitic and pro-eutectoid cementite to merge together (overheated steel).

(*f*) In iron-carbon alloys not in equilibrium; in quenched white irons, and particularly in quenched hyper-eutectoid steels, if the quenching temperature has not been sufficiently high, the time heated not sufficient, or the rate of cooling too slow. The structures will approximately correspond with those previously described, but the structure may or may not be partly destroyed by partial solution during the heating and quenching.

Pearlite

Definition.—Eutectoid of alpha iron (ferrite) and Fe_3C (cementite) consisting of 6 parts of iron to 1 part of Fe_3C and containing 0·9 per cent. C. It is therefore a conglomerate of fixed chemical composition and constitution, consisting of alternate lamellæ of ferrite and cementite (Figs. 227–228, Pl. XXXVI., p. 137): *lamellar pearlite.* Coalescence of the cementite, brought about by the conditions of cooling or further heating below 700° C., will cause the formation of extremely fine globules of cementite immersed in the ferrite, *granular pearlite* (Figs. 270–273, Pl. XLVII., p. 144).

Etching.—Pearlite is attacked and coloured by any of the usual acid reagents (Picric acid, Bénédick's reagent, nitric acid, *see* Figs. 258–267, Pl. XLIV., XLV., XLVI., p. 144); it is more readily stained than martensite, but less readily than troostite, sorbite, and osmondite. Under higher magnification (250 diams. minimum) it may be resolved into a series of fine lamellæ, but pearlite in overheated steels may often be distinguished with as low a magnification as 25 diameters. The more rapidly the pearlite has been formed, the finer will be its structure and the higher the magnification required for its resolution (certain special elements, such as nickel and chromium, increase the fineness of the structure).

It should be observed that the coloration of pearlite is only an effect of shadow and relief, since the two constituents of the conglomerate ferrite and cementite are not stained by the reagents that darken the pearlite; the etching accentuates the relief of the cementite. To the eye, etched pearlite presents a similar appearance to mother-of-pearl, the appearance of which is also due to a lamellar structure, hence the name *pearlite* given by Sorby to this constituent. The coloration varies with the distance of separation between the bands of cementite and ferrite, and this separation is dependent on the thickness of the lamellæ and the plane of the section.

Structure.—*Lamellar Pearlite.*—Polishing in relief followed by etching reveals the pearlite as alternate lamellæ of ferrite and cementite, the thickness of the lamellæ being dependent on the conditions of cooling and the other elements present in the alloy (Figs. 227–228, Pl. XXXVI., p. 137). In practice, under the usual conditions of manufacture, the pearlite of hyper-eutectoid steels is more easily resolved than that of hypo-eutectoid steels. Each cluster of parallel lamellæ is a " grain " of pearlite.

Granular pearlite (Fig. 99, Pl. XII., p. 78 ; Figs. 270–272, Pl. XLII., p. 144).—This form results from the coalescence of the cementite of the lamellar pearlite either during the formation of the pearlite or during subsequent heating in the ferrite-cementite area at as high a temperature as possible but below 700° C. The conversion of lamellar to granular pearlite will be preceded, according to Bénédicks, by a condition where the cementite will exist as chains of minute globules.

Pearlite, being formed after the other constituents, will constitute the ground mass, and its form and outline will be dependent on the other constituents.

Graphite

Definition.—Free elemental carbon which occurs in iron and steel.

Properties.—When isolated it is found to be identical with pure graphite ; brittle, it is frequently partially removed by the polishing operations leaving cavities. The colour varies from black to dark grey. Sp.gr. 2·25 ; it may be isolated from steels and estimated by analytical methods. After isolation it may be oxidised by suitable reagents to carbon dioxide.

Etching.—Graphite appears as black areas after polishing and without etching. Etched specimens, if not thoroughly washed, frequently retain some of the reagent in the graphite areas or cavities ; on drying the specimen, this remaining liquid creeps over the specimen causing staining round the edges of the cavities.

Structure.—(*a*) *Graphite separating from liquid cast iron* appears as thin plates, usually curved, which may be several millimetres in length (Fig. 231, Pl. XXXVII., p. 142).

(*b*) *Temper graphite* or *temper carbon*, resulting from the decomposition of metastable cementite during annealing, appears as small, black, rounded particles or points surrounded by ferrite. It is also produced by the decomposition of Fe_3C (Fig. 379, Pl. LXXI., p. 184). Graphite and ferrite are sometimes distributed in a manner which suggests the formation of the eutectic of the stable equilibrium diagram (Fig. 232, Pl. XXXVII., p. 142).

Austenite

Definition.—Solid solution of iron and carbon retained in unstable equilibrium at ordinary temperatures. In carbon steels it is never obtained in the pure state, martensite always being present. Its carbon content is variable.

Properties.—Isometric (Osmond), rhombohedral (Le Chatelier). Octahedral cleavage: softer than the martensite with which it is associated. Specific magnetism very slight, very ductile.

Etching.—It is attacked by any of the usual acid reagents to a less extent than troostite and sorbite and a greater extent than cementite. It is generally less affected than martensite (Fig. 235, Pl. XXXVIII.), and rarely appears darker than that constituent; martensite may be distinguished from austenite by its acicular or needle-like structure and its greater hardness as found by a needle scratch.

Structure.—In carbon steels, since austenite is always associated with martensite, the mixture of these two constituents will be examined; this mixture has a characteristic appearance, the martensite occurring in the form of needles, arrow heads or zigzags in a background consisting of austenite (Fig. 235, Pl. XXXVIII.).

The mixture may constitute the entire mass of the steel or be associated with pro-eutectoid or eutectic cementite.

The polyhedral structure of austenite is only to be observed in certain special steels which may be obtained in the pure austenitic form (Fig. 236, Pl. XXXVIII.). It is frequently twinned and readily develops slip bands.

Martensite

Definition.—Transitional constituent indicating the first stage of the decomposition of austenite. It is characterised by the return of magnetic properties, great hardness, and an acicular structure (frequently indiscernible).

Its constitution has not been definitely decided; there appears to be little doubt that the iron exists partially in the alpha condition, under strain, and that carbon is retained in solid solution.

Its carbon content is variable.

Properties.—Its hardness is greater than that of any of the other constituents of the same carbon content; its specific hardness and brittleness are dependent on its carbon content and increase with this content up to 0·9 per cent. C. Magnetic. It is frequently intermixed with other constituents, such as austenite in greater or less proportion; its properties cannot therefore be exactly defined.

Etching.—The usual acid reagents attack this constituent more readily than ferrite and cementite, but less readily than troostite,

CONSTITUENTS OF IRON-CARBON ALLOYS.

Graphite.

FIG. 231.—Primary graphite and eutectic graphite in a cast iron, 4·98 % C., unetched. (BÉNÉDICKS.) (× 27.)

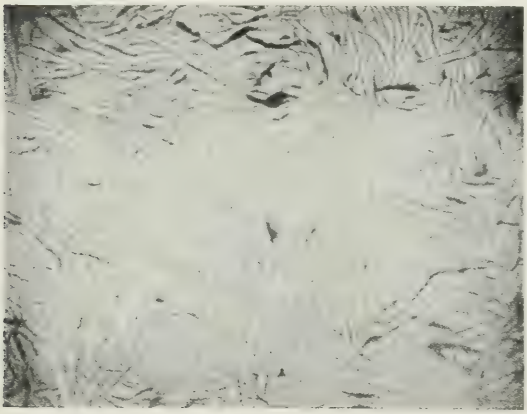


FIG. 232.—Eutectic graphite; unetched. (BÉNÉDICKS.) (× 27.)

CONSTITUENTS OF HARDENED STEELS.

Unstable and transitional constituents.

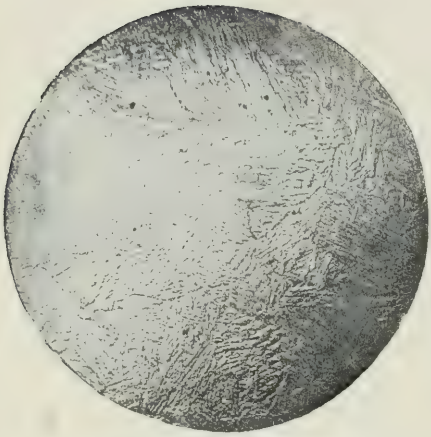


FIG. 233.—Pure Martensite. Steel quenched from a high temperature.
Etchant: Picric acid.
(× 200.)

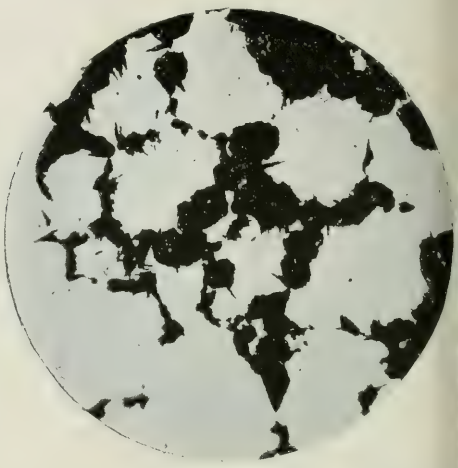


FIG. 234.—Troostite (black). Steel quenched fro a temperature below the upper critical point.
Etchant: Picric acid.
(× 200.)

FIG. 235.—Austenite-martensite.
Severe quenching.
Etchant: Picric acid.
(× 200.)

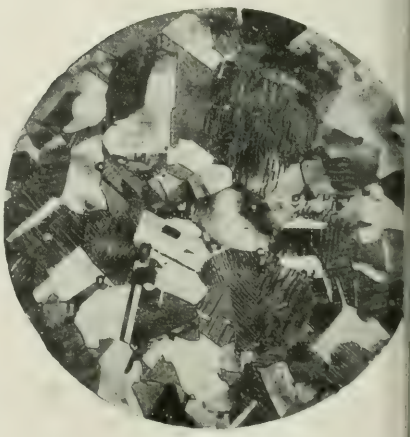


FIG. 236.—Special steel, showing pure austenite.
Etchant: Picric acid.
(× 200.)

sorbite and osmondite (Figs. 241–243, Pl. XL., p. 144 ; Fig. 286, Pl. LI. ; Fig. 315, Pl. LX., p. 144). As a general rule it appears darker than austenite after etching (refer to the etching of austenite).

It may also be identified by its hardness (it is not scratched by a needle).

Structure.—When pure, martensite has an acicular or needle-like structure (Fig. 233, Pl. XXXVIII. ; Fig. 238, Pl. XXXIX., p. 144), the needles being frequently arranged in three principal directions. The structure is in some instances so fine that the needles are indiscernible. Under similar conditions, martensite is more readily stained or attacked the greater the carbon content. When of constant carbon content it is more readily attacked as the transformation is more advanced (*see* later : osmondite). Characteristic specimens may be obtained by quenching 1 cm. square bars of eutectoid steel containing 0·9 per cent. C in cold water from 800° C. (1472° F.).[1]

Its form or outline is dependent on the crystalline form of the austenite from which it is derived.

The orientation of the needles corresponds to the cleavage planes of austenite,[2] the structure is therefore allied to the Widmanstaetten structure.

Troostite, Osmondite, Sorbite

Definition.—The transitional constituents which, together with martensite, represent the distinctive changes occurring during the austenite→pearlite transformation ; their respective positions in the chain are :

austenite → martensite → troostite → osmondite → sorbite → pearlite

These products are obtained successively either by quenchings progressively less severe or by annealing quenched steels at increasing temperatures. Under such conditions a gradual change from one constituent to the next will be observed. Osmondite is assumed to be an arbitrary boundary existing between troostite and sorbite.

These three constituents are not in structural equilibrium but are probably in physcio-chemical equilibrium.

Osmondite has been defined by the Congress of the Association for Testing Materials at Copenhagen as follows :—

" Osmondite, the exact nature of which is still a debated point, is an intermediate stage in the return of martensite to the pearlitic condition, the latter being the stable form at ordinary temperatures. It is considered as a distinct constituent, because of the rapid alteration in the rate of variation of certain of the properties of the metal

[1] Martensite is always produced when the rate of quenching exceeds the " critical speed " (Portevin et Garvin, *C. R.*, 164, 885 , 1917).

[2] *See* Portevin, *C.R.*, 165, 62 ; 1917.

during the transformation between the two extreme conditions of the metal. It is characterised by its maximum solubility in acids and by a maximum coloration under the action of acid metallographic reagents.

"It may be obtained, other conditions being favourable, by annealing martensitic eutectoid carbon steel (0·9 per cent.) at 400° C."

These constituents are not resolved by the highest magnifications at present available. The distinction between the three constituents is slight and is frequently disregarded.

Properties and Etching.—It is obvious that the properties of these constituents will vary with their carbon content and the stage in their transformation to the pearlitic condition. For any given carbon content, the hardness, electrical resistance, and thermo-

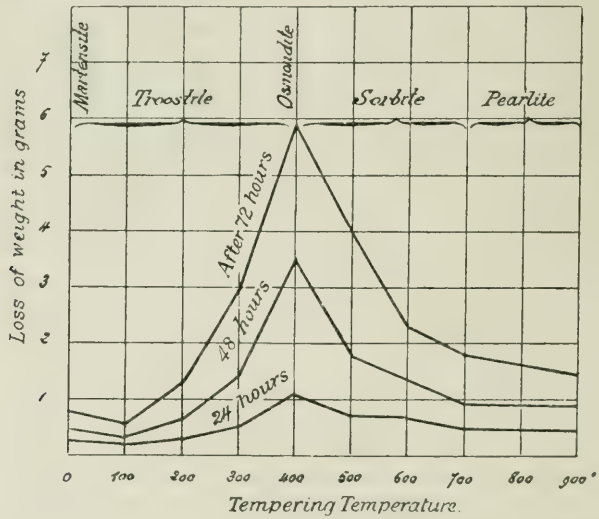


FIG. 244 (Heyn).

electric power decrease continuously during the passage from martensite to pearlite; on the other hand, the minimum brittleness is obtained in the sorbitic condition.

If a steel containing 0·9 per cent. C is obtained in the martensitic condition by quenching from 900° C. and is then submitted to a series of annealings of increasing intensity, it is found that as a function of the carbon content (Heyn) :—

1. The solubility in 1 per cent. sulphuric acid has a maximum value clearly indicated (Fig. 244).

2. The coloration after etching in 1 per cent. hydrochloric acid in alcohol also shows a maximum (Fig. 244, Pl. XL.).

These two experiments afford a definite definition for osmondite and at the same time show the relative colorations produced on the various transitional constituents of steel.

CONSTITUENTS OF QUENCHED STEELS—TROOSTITE, MARTENSITE, AND AUSTENITE.

The same field after varying periods of etching.

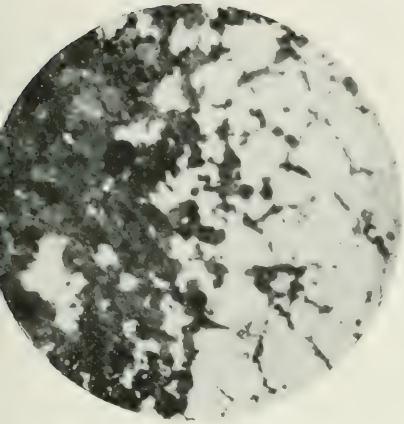


FIG. 237.—Three minutes' etching in picric acid.

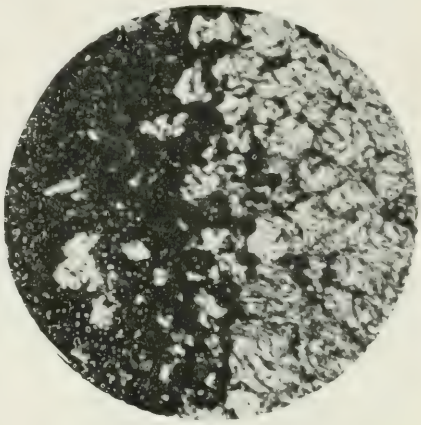


FIG. 238.—Sixty minutes' etching in picric acid.

The troostite is discoloured by a slight etching, the martensite remaining unattacked; the prolongation of the etching shows up the acicular structure of the martensite.

The same specimen viewed under different magnifications.

Etchant: Picric acid.

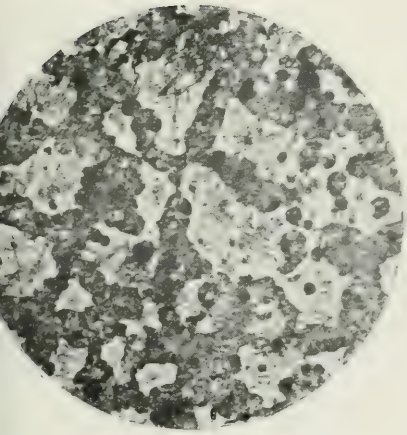


FIG. 239.—Troostite, the darker constituent. (× 50.)

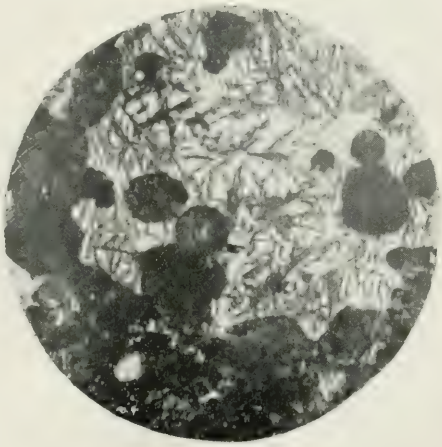


FIG. 240.—At higher magnifications the lighter constituent shows the characteristic structure of austenite-martensite. (× 200.)

DIFFERENTIAL ETCHING OF THE VARIOUS CONSTITUENTS OF QUENCHED CARBON STEELS.

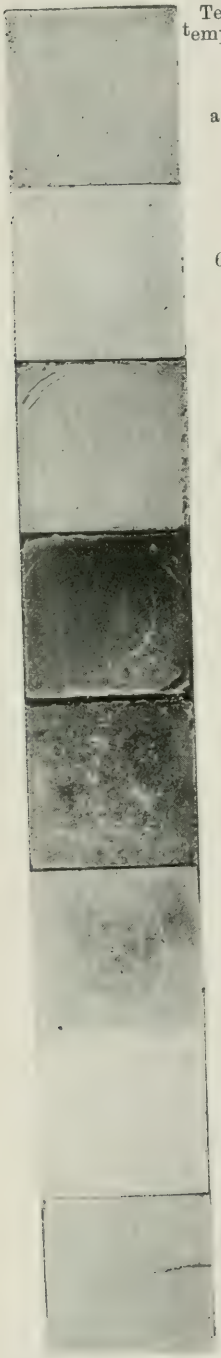


FIG. 241.—0·95 % C. steel, water quenched at 900° C., and tempered at various temperatures. Etchant: 1 % hydrochloric acid in alcohol for 10 minutes. (HEYN & BAUER.)

FIGS. 242–243.—Martensite, troostite, ferrite, and pearlite in a medium carbon steel quenched in oil from 850° C.

Etchant: Bénédicks' reagent.

White areas of martensite surrounded by dark areas of troostite in a background of ferrite-pearlite.

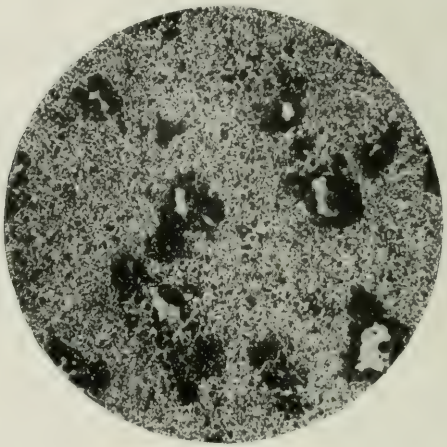


FIG. 242.
(× 57.)

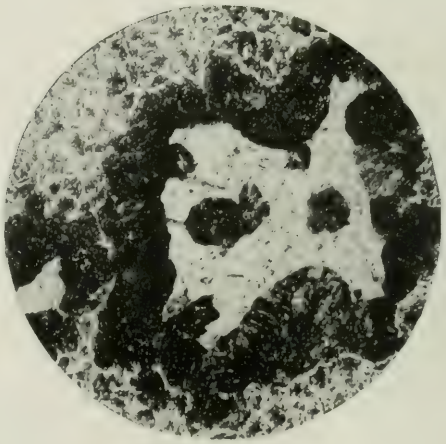


FIG. 243.
(× 200.)

SLAG INCLUSIONS IN PUDDLED IRON.

In the larger inclusions it is often possible to distinguish several different constituents of the slag either before or after etching.

1° Unetched.

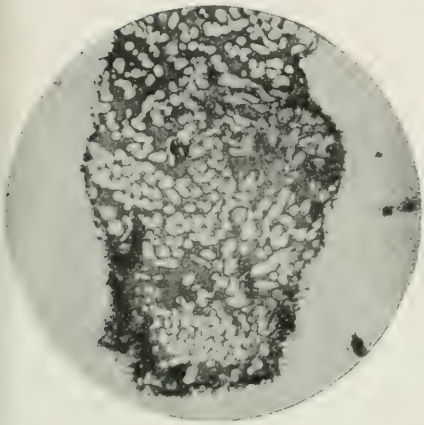


Fig. 245.
(× 200.)

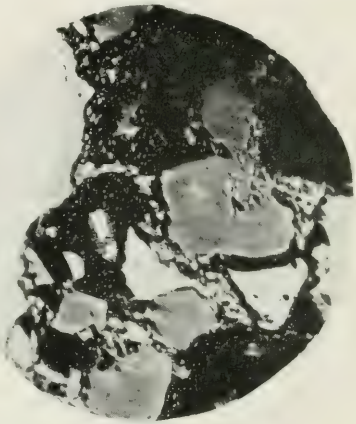


Fig. 246.
(× 550.)

2° After etching.
Etchant: Bénédicks' reagent.

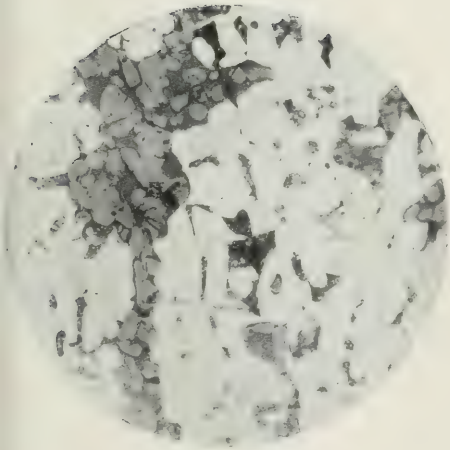


Fig. 247.
(× 200.)

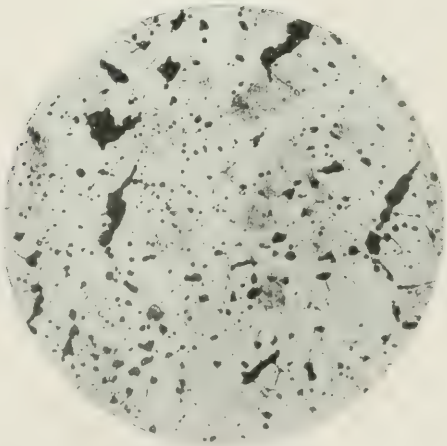


Fig. 248.
(× 200.)

INCLUSIONS IN HYPOEUTECTOID STEELS.

(× 200.)

Unetched.
Showing only inclusions.

The same field after etching with picric acid.
Pearlite, dark; inclusions, dark; ferrite, white.

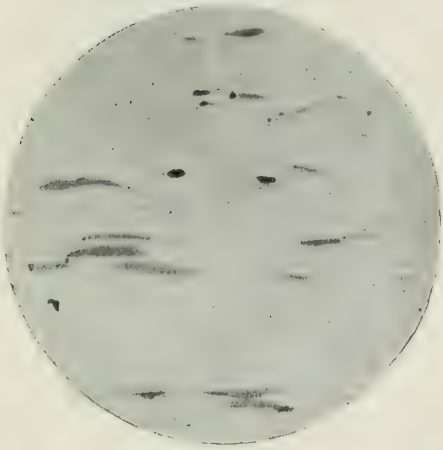


Fig. 249.

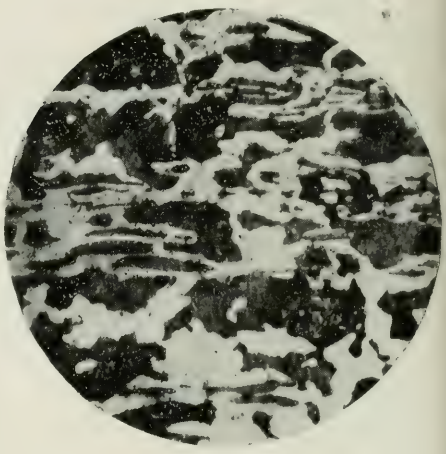


Fig. 250.

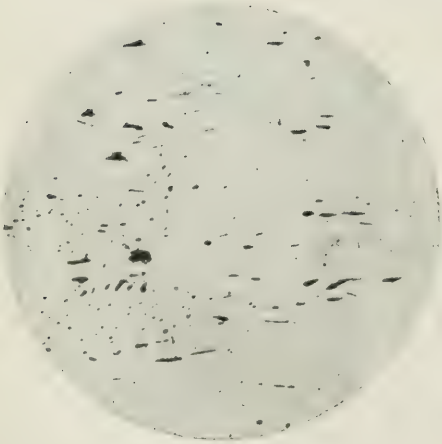


Fig. 251.

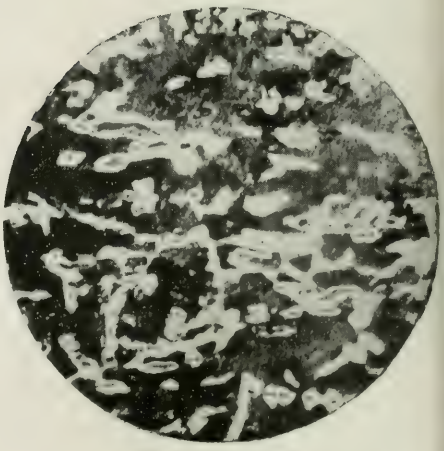


Fig. 252.

Longitudinal sections.
Showing orientation of the inclusions due to rolling.

INCLUSIONS IN IRON AND STEEL.

1° Inclusions in iron.

(× 200.)

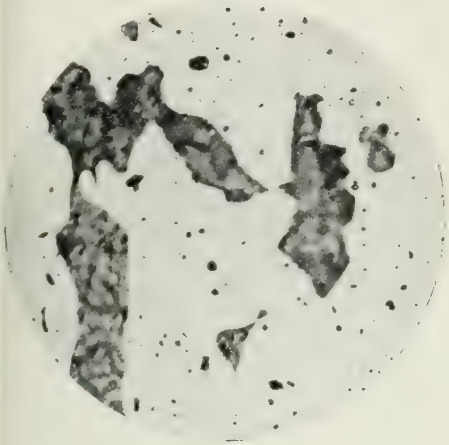


Fig. 253.—Unetched.

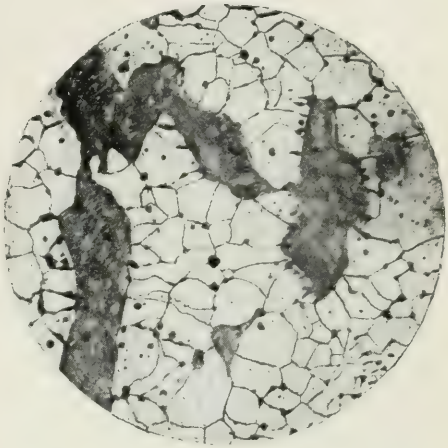
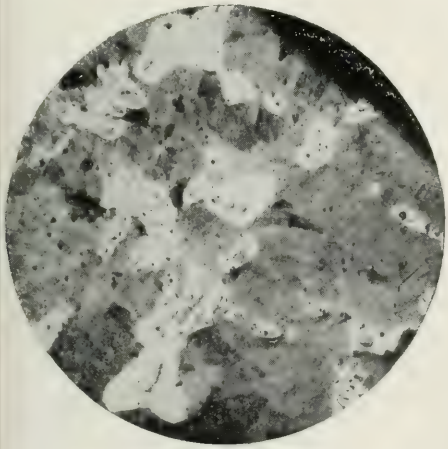


Fig. 254.—Same field etched with picric acid.—Showing the ferrite crystal boundaries.

2° Inclusions in steel.

Etchant: Picric acid.



White areas of ferrite surrounding the inclusions (manganese sulphide); background of dark pearlite.

Fig. 255.
(× 50.)

Fig. 256.—Same field; higher magnification.
(× 200.)

APPROXIMATE ESTIMATION OF THE CARBON CONTENT OF ANNEALED HYPOEUTECTOID STEELS.

Ferrite, white; pearlite, dark.

Etchant: Bénédicks' reagent.
(× 200.)

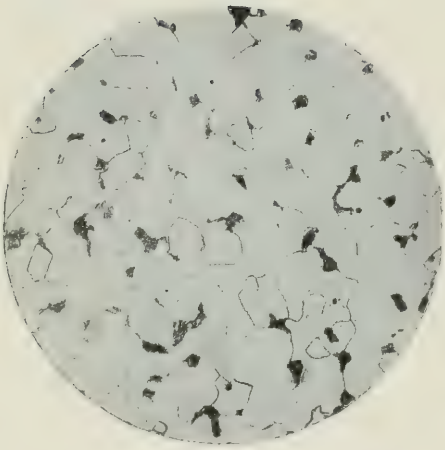


FIG. 258.—0·10 % C. steel annealed at 900° C.

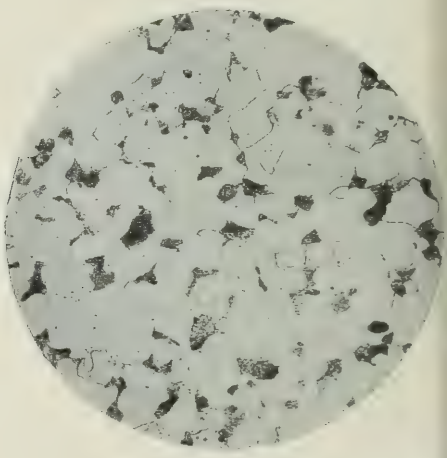


FIG. 259.—0·19 % C. steel annealed at 850° C.

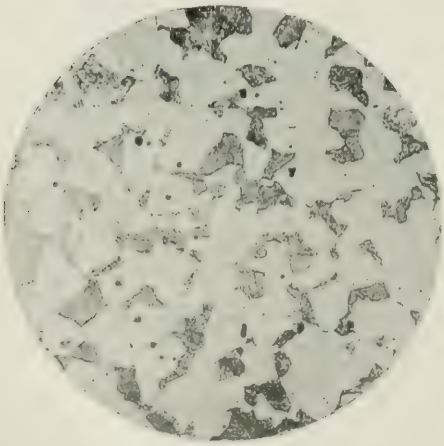


FIG. 260.—0·24 % C. steel annealed at 850° C.

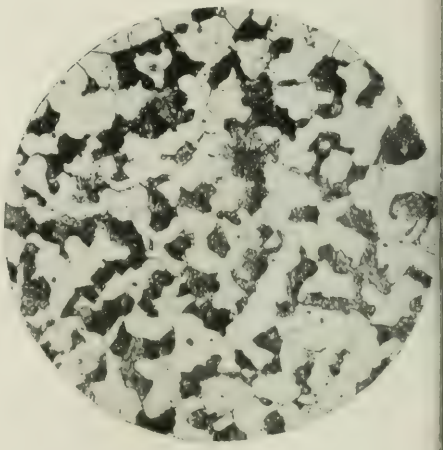


FIG. 261.—0·33 % C. steel annealed at 850° C.

APPROXIMATE ESTIMATION OF THE CARBON CONTENT OF ANNEALED HYPOEUTECTOID STEELS (*contd.*).

Ferrite, white ; pearlite, dark.

Etchant : Bénédicks' reagent.
(× 200.)

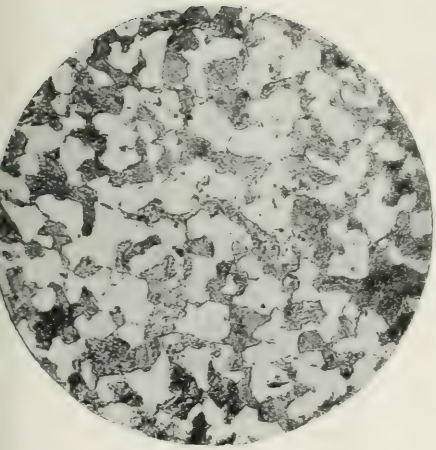


FIG. 262.—0·44 % C. steel annealed at 850° C.

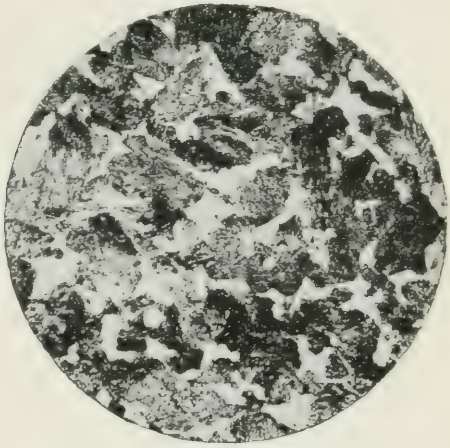


FIG. 263.—0·54 % C. steel annealed at 850° C.

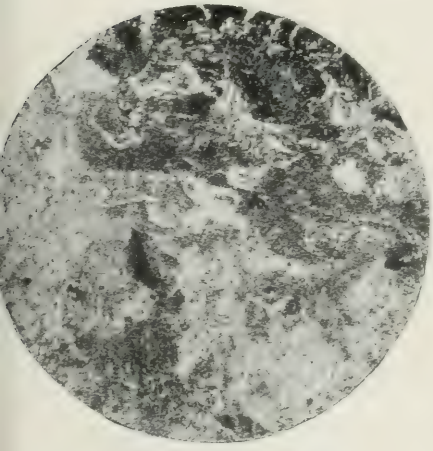


FIG. 264.—0·64 % C. steel annealed at 850° C.

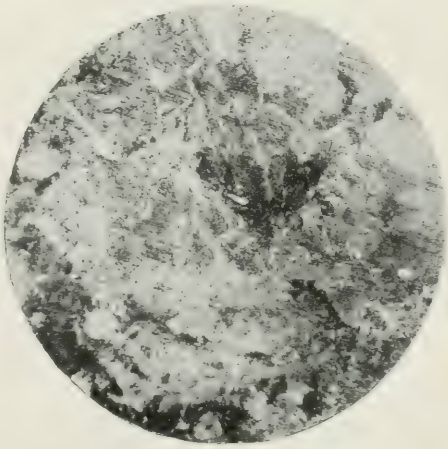


FIG. 265.—0·70 % C. steel annealed at 850° C.

APPROXIMATE ESTIMATION OF THE CARBON CONTENT OF ANNEALED HYPOEUTECTOID STEELS (*cont.*).

Ferrite, white; pearlite, dark.

Etchant: Bénédicks' reagent.
(× 200.)

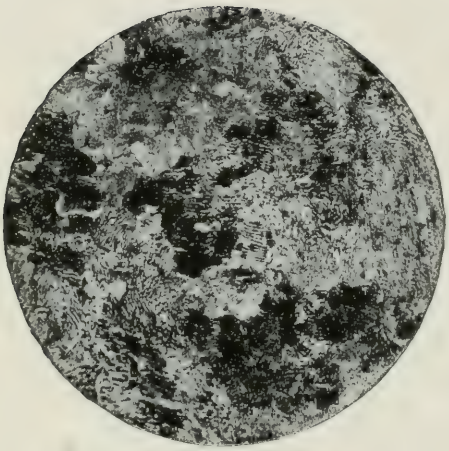


FIG. 266.—0·77 % C. steel annealed at 850° C.

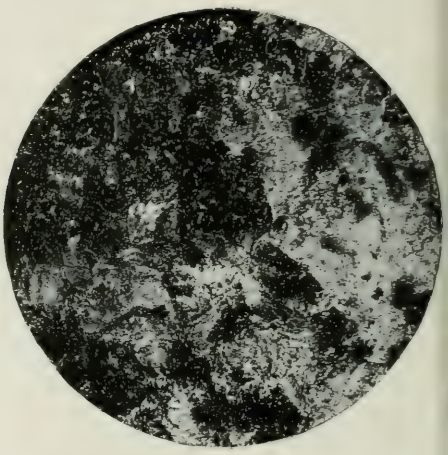


FIG. 267.—0·80 % C. steel annealed at 850° C.

ORDINARY HYPEREUTECTOID CARBON STEELS AFTER FORGING.

(× 200.)

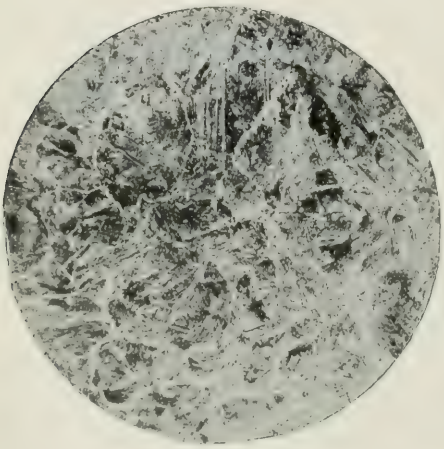


FIG. 268.—1·43 % C. steel (Mn = 0·29; Si = 0·15). Transverse section.
Etchant: Bénédicks' reagent. White needles and meshwork of cementite; pearlite, dark.

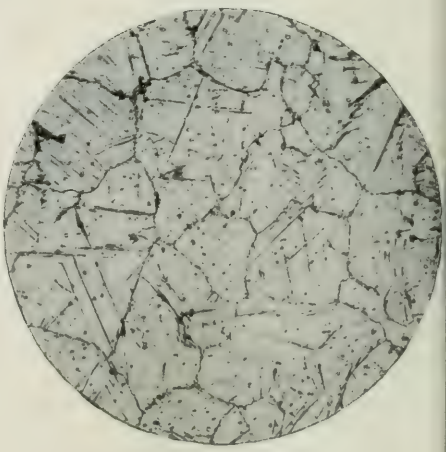


FIG. 269.—1·43 % C. steel (Mn = 0·29; Si = 0·15). Transverse section.
Etchant: Sodium picrate. Dark needles and meshwork of cementite; pearlite, white.

ORDINARY HYPEREUTECTOID STEELS ANNEALED AT 850° C.

The effect of annealing is shown by the coalescence of the cementite, the pearlite no longer exhibiting its characteristic structure.

(× 200.)

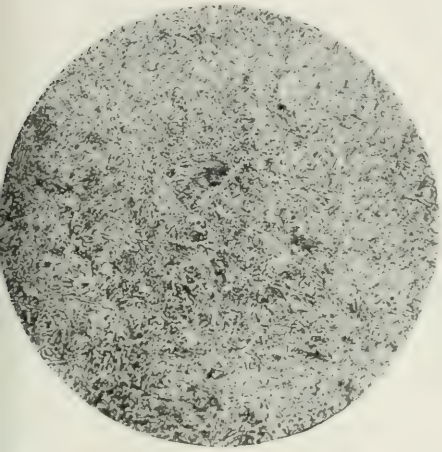


FIG. 270.—1·40 % C. steel.
Etchant: Bénédicks' reagent.
Cementite remains white.

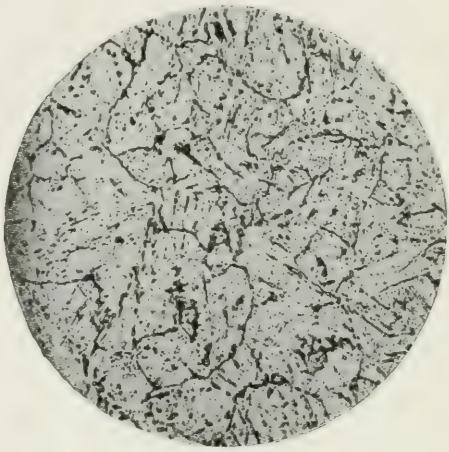


FIG. 271.—1·40 % C. steel.
Etchant: Sodium picrate.
Cementite is darkened.

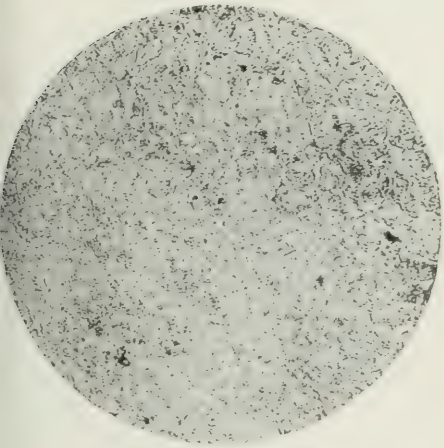


FIG. 272.—1·60 % C. steel.
Etchant: Bénédicks' reagent.
Cementite, white.

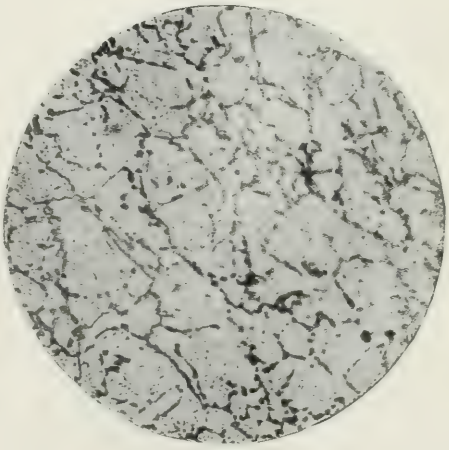


FIG. 273.—1·60 % C. steel.
Etchant: Sodium picrate.
Cementite, dark.

EFFECT OF ANNEALING ON THE DISTRIBUTION OF THE CONSTITUENTS.

1° Cast steel.

Etchant: Picric acid.
(× 200.)

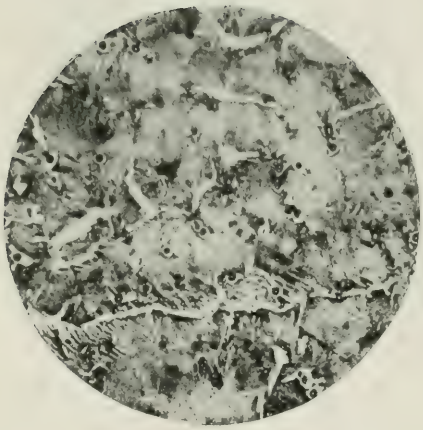


FIG. 274.—As cast.

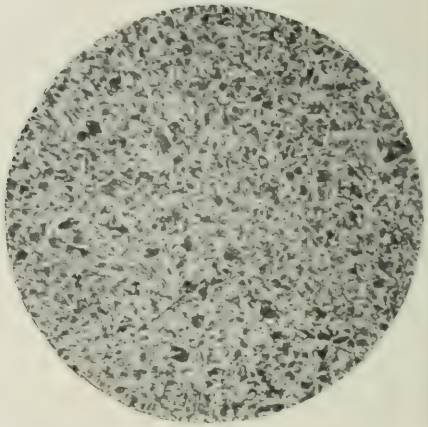


FIG. 275.—Annealed.

2° Forged steel.

Etchant: Picric acid.
(× 200.)

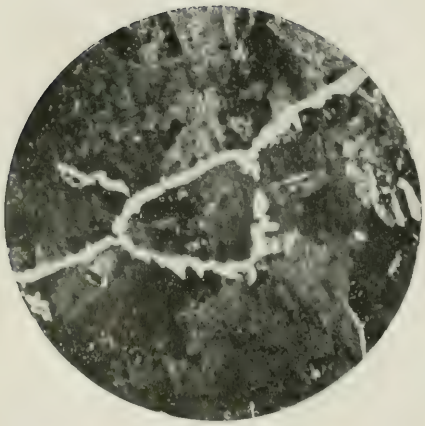


FIG. 276.—As forged.

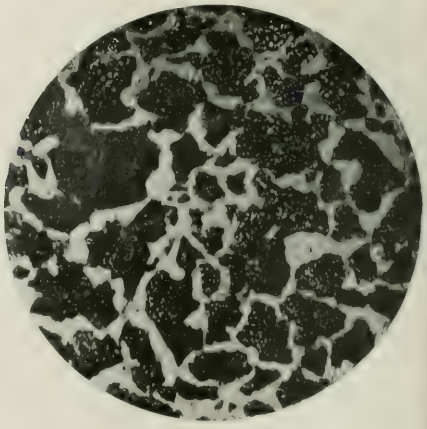


FIG. 277.—Annealed.

DISTRIBUTION OF THE CONSTITUENTS FERRITE AND PEARLITE IN HYPOEUTECTOID STEELS.

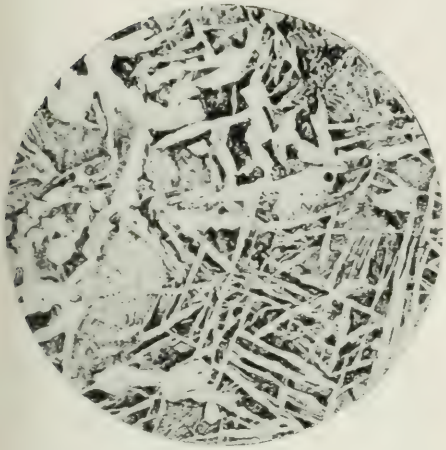


FIG. 278.—Medium carbon steel as forged.
Widmanstaetten structure.
Etchant: Bénédicks' reagent.
(× 75.)

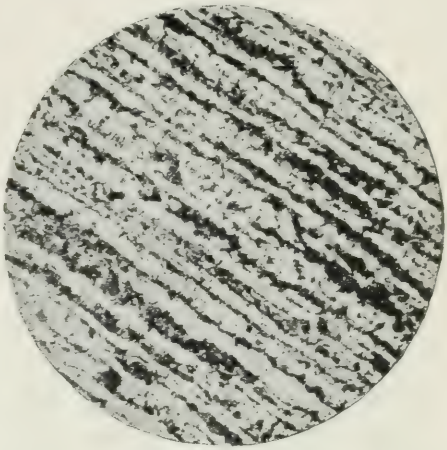


FIG. 279.—Steel.
(C = 0·29 ; Cr = 0·93 ; Mn = 0·33 ; Ni = 0·16)
annealed.
Banded structure.
Etchant: Bénédicks' reagent.
(× 80.)

Silico-manganese steel after prolonged annealing at 900° C.

Banded structure.

Etchant: Bénédicks' reagent.

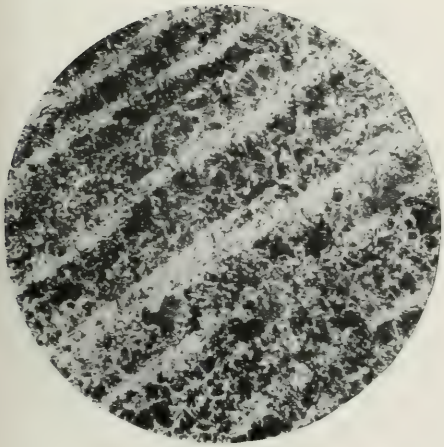


FIG. 280.
(× 57.)

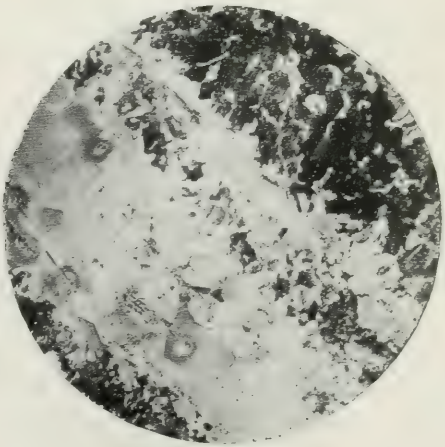


FIG. 281
(× 200.)

EFFECT OF MECHANICAL DEFORMATION AND HEAT TREATMENT ON CARBON STEELS.

1° Effect on the ferrite-pearlite structure.—Tensile test-piece.

Etchant: Picric acid.
(× 200.)

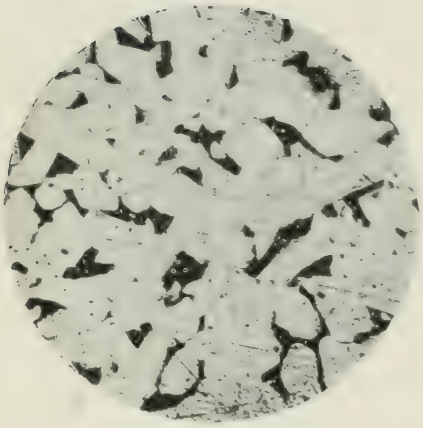


FIG. 282.—Before testing.

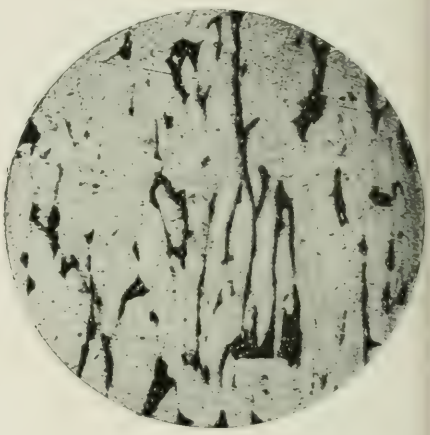


FIG. 283.—After testing.

2° Effect on the ferrite grains.

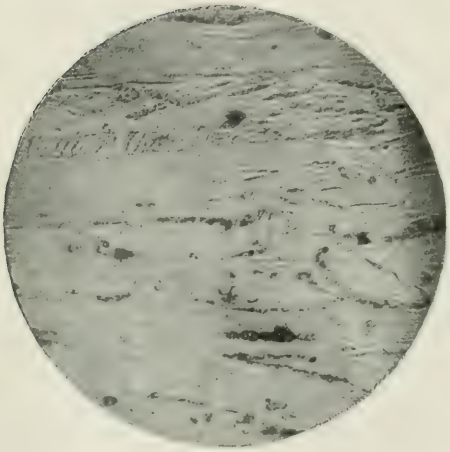


FIG. 284.—Thin drawn mild steel.
Etchant: Bénédicks' reagent.

FIG. 285.—Pure iron, polished, and afterwards heated in hydrogen.
Meshwork structure.

The three constituents possess the following distinguishing properties :—

1. Very rapid coloration with the ordinary acid reagents.

2. Their structure is not resolved even under the highest magnifications.

The first property permits them to be distinguished from ferrite, austenite, and martensite (Figs. 242, 243, Pl. XL.). The second distinguishes them from pearlite (and also from martensite, which under high magnifications exhibits an acicular structure).

The methods of distinguishing between sorbite and troostite may be summarised as follows :—

(*a*) **Etching and Appearance.**—According to Kourbatoff, after seven minutes' etching in the reagent suggested by him (*see* p. 10), only troostite will be coloured, the other constituents remaining unaffected. Troostite is usually associated with martensite, and frequently appears as small rounded masses in the form of chains (Fig. 234, Pl. XXXVIII., p. 143, and Figs. 237–240, Pl. XXXIX.).[1] It is the constituent produced by a mild form of quenching. Sorbite is usually associated with pearlite, and appears as irregular-shaped plates or masses. It is the constituent normally produced by rapid annealing.

(*b*) **Production or Formation.**—Troostite appears on annealing martensite a little below 400° C. ; by quenching small specimens in the middle of the transformation area, and in the interior of large specimens quenched above the transformation temperature. It is therefore produced by quenching at speeds below the "critical speed." [2]

Sorbite appears on annealing above 400° C. but below 700° C. ; by quenching in water just above the lower limit of the transformation area A_1 ; by quenching small specimens in oil, molten lead, or even air.

Inclusions

Definition.—Inclusions are the impurities present in iron-carbon alloys which are insoluble in these alloys at ordinary temperatures, and may be seen by microscopical examination before etching (Figs. 249 and 251, Pl. XLII., and Fig. 253, Pl. XLIII.).

Composition.—The inclusions consist of: oxides of iron and manganese ; sulphides of iron and manganese ; silicates of iron and manganese ; phosphides of iron.

Appearance.—Inclusions of various shapes may be seen after polishing : spots (Fig. 248, Pl. XLI. ; Fig. 251, Pl. XLII.), rounded

[1] It is produced by rates of cooling intermediate between that required for the formation of martensite and that for the visible separation of cementite and ferrite ; it frequently appears, as already stated, as a border, surrounding the martensite areas and separating them from the cementite or ferrite areas when these are present.

[2] *See* Portevin and Garvin, *C. R.*, 164, 885, 1917.

masses (Figs. 255, 256, Pl. XLIII.), areas, elongated in the direction of rolling (Fig. 249, Pl. XLII.), of irregular shape (Fig. 247, Pl. XLIII. ; Figs. 253, 254, Pl. XLII.). Their collection in bands has a particularly injurious effect on the mechanical properties of steel (ghost lines).

They vary in colour, and may be grey, black, fawn, brown, and sometimes blue (dove-grey or slate colour=MnS). In the larger slag inclusions it is frequently possible to distinguish several different constituents after etching (Figs. 245–247, Pl. XLI. ; Figs. 253, 254, Pl. XLIII.).

Etching and Identification.—(*a*) The areas containing sulphur in the form of FeS or MnS may be revealed macrographically (*see* Chap. VI.) by means of silk impregnated with bi-chloride of mercury and sulphuric acid (Heyn and Bauer), or by bromide paper moistened with hydrochloric acid (Baumann). The material applied to the polished surface of the metal is locally darkened where it comes in contact with the sulphide areas (the phosphide areas also darken bromide paper).

(*b*) *Matweieff's Method.*—By the use of hot gaseous reagents it is possible to observe the reaction or reduction (by hydrogen) of the various inclusions. The reduction is verified, after experiment, by repolishing the specimen, when the inclusion should disappear.

1. Substances not affected by hydrogen at 300° C., superheated steam, or weak organic acids : silicates of iron and manganese.

2. Substances reduced to the metallic state by hydrogen at 300° C., etched by steam but not by weak organic acids : oxides of iron and manganese.

The presence of manganese is verified by the discoloration produced on etching with a weak alcoholic solution of ferric chloride after reduction and repolishing.

3. Substances not attacked by hydrogen or steam, but attacked by weak organic acids (tartaric acid) : sulphides of iron and manganese, the first being the more rapidly coloured by tartaric acid.

(*c*) Phosphide is met with more particularly in cast irons (Pl. LVIII., p. 153), where it forms a triple eutectic with the cementite and the solid solution (subsequently transformed to pearlite). It is coloured by sodium picrate in a similar manner to cementite but less rapidly, and is unaffected by the ordinary acid reagents.

Heat tinting may be used to distinguish cementite from phosphide, the cementite being more rapidly coloured and oxidised than the phosphide.

Distribution of Inclusions.—Macrographic examination shows the distribution of the inclusions to be mainly dependent on : the conditions of cooling in cast metal ; the mechanical treatment (hot) in the case of forged or rolled metal. These conclusions help to

explain the occurrence of such inclusions as lines or bands, which are particularly noticeable with manganese sulphide (ghost lines).

Microscopically the inclusions are generally found to occur in the pro-eutectoid constituents: ferrite or cementite. According to Ziegler it is these inclusions which determine the method of separation of the ferrite and cementite, the inclusions producing a similar effect on solid solutions as small particles of foreign substances produce on the crystallisation of salts from aqueous solutions. The network of slag governs the formation of the network of ferrite; and since this slag constitutes a line of weakness of the material as regards resistance to deformation and shock, it explains the occurrence of cracks along the ferrite network.

In the case of the oxidised impurities (slag, oxides), the oxidising and reducing actions interfere with the production of this effect (Giolliti and Zablena).

In forged steel the distribution of the inclusions as bands assists the elongated structure of the ferrite and pearlite, and offers an explanation as to why this structure is accentuated by annealing. But, as one of the authors has suggested,[1] this phenomenon may also be explained by the liquation of the ferrite in the solid state in a heterogeneous solid solution due to the conditions of solidification.

Structure of Steels and Cast Irons

Having now considered the constituents of steel, their principal characteristics, and also the conditions that are favourable to the production of these respective constituents, it is possible to form an estimate of the structure of the iron carbon alloys.

The examination of the structure of these alloys is best considered under two headings:

1. Chemical constitution, which includes the nature of the constituents, and is in turn dependent on the chemical composition (carbon content) and heat treatment.

2. Physical constitution, which includes the size and distribution of the constituents, and is dependent on the conditions of solidification, heat treatment, and mechanical treatment.

In the following description steels and cast irons are considered separately for the following reasons:—

1. Cast iron undergoes no mechanical treatment such as rolling, forging, etc. Therefore it is only necessary to examine the conditions of casting and heat treatment, whereas with steels the changes produced by mechanical treatment must also be considered.

2. From a practical standpoint (commercial use), the occurrence

[1] Portevin, *Revue de Met.*, vol. x. p. 689, 1913.

of graphite and the stable equilibrium conditions are only met with in cast irons.

Stable equilibrium will not be considered in the case of steel.

A. Steels

Steels are classified into two classes according to their chemical constitution and the constituents present:

1. Annealed steels—as cast, or cast and annealed.
2. Quenched, or quenched and tempered steels.

Steels of the first class may again be subdivided into two classes, according to the distribution and size of the individual particles of the constituents. Type of structure:

1A. Steels as cast which have undergone no mechanical treatment after solidification.

1B. Steels that have been forged, stamped, rolled, etc., but not heat treated.

1. **Annealed steels.**—There are only three possible constituents: ferrite, pearlite, cementite.

Excepting overheated steels (considered later), where the annealing or cooling has been greatly prolonged, the only possible combinations that occur are:—

pro-eutectoid ferrite + pearlite
pro-eutectoid cementite + pearlite

and the alloy containing 0·89 per cent. C, eutectoid steel, consisting of pure pearlite.

The proportions of ferrite and pearlite, or cementite and pearlite present permit a rough approximation of the carbon content to be made in the manner previously indicated (p. 74).

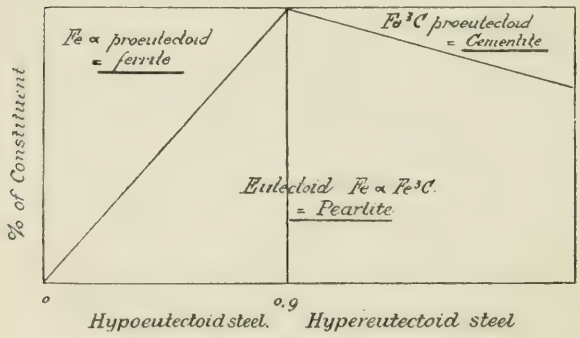


FIG. 257.

The diagram (Fig. 257) shows the proportions of the two constituents present for any definite composition. It will be observed that this method of estimation is more accurate for hypo-eutectoid steels than for hyper-eutectoid steels. This is explained by the fact that the proportion $\frac{\text{ferrite}}{\text{pearlite}}$ changes in the first case from 100 to 0 per cent. as the carbon content increases from 0·0 to 0·9 per cent. C,

whilst the proportion $\frac{\text{cementite}}{\text{pearlite}}$ changes from 0 to 100 per cent. as the carbon content increases from 0·9 to 6·6 per cent. C.

In practice it is only possible to estimate the carbon content in *fully annealed hypo-eutectoid steels.*

The micrographs (Figs. 258–267, Pls. XLIV., XLV. and XLVI. at p. 144) may be used as a guide in making estimations of this nature.

It must be observed that in estimating the carbon content by this method it is essential that the annealing conditions shall be the same in every case. The rate of cooling greatly affects the segregation of the pro-eutectoid ferrite, an increase in the rate of cooling tending to decrease the area occupied by the ferrite. This method of estimation is also affected by the presence of various other elements (Mn, Si, etc.). The magnification chosen must be such that the image obtained approximately corresponds with the test diagram.

The carbon content can be estimated to within 0·1 per cent. in the case of hypo-eutectoid steels. In spite of the fact that this method does not compare in accuracy with chemical analysis, it offers the advantage that an approximate estimation can be rapidly made on very small samples. An interesting application of the method is found in estimating case hardening and decarburisation (p. 156).

This method, which instead of estimating the relative amounts of the constituents in a given volume of the material, estimates them in a given plane, requires, as an essential condition of accuracy, that the various constituents shall be evenly distributed throughout the mass ; hence the necessity, in the case of rolled steels, of examining a transverse as well as a longitudinal section.

The constituents and their relative proportions having been described, their *distribution* will now be considered.

1A. **Steels, as cast.**—In accordance with the general conditions described in Chap. II. :—

(1) On solidification, the solid solution crystallises in the form of dendrites and is chemically heterogeneous, since equilibrium is never attained in practice ; the mutual limitations of the dendrites outline the crystal grains ; these grains and dendrites are, in the case of chill castings, elongated and developed around a peripheral zone, normal to the inner face of the mould. Macroscopic etching for several hours in 2 per cent. picric acid or etching with the Stead-Le Chatelier reagent (see Chap. VII.) reveals the dendritic structure which is visible owing to the unequal distribution of carbon due to the heterogeneous solidification of the solid solution.[1]

[1] This is the structure termed " large crystals " by N. J. Bélaiew (*see* Chap. VII.)

This chemical heterogeneity persists even after heat treatment, quenching, annealing, tempering; the macrostructure, therefore, always remains the same and is only changed by mechanical treatment (*see* Chap. VII.).

(2) On passing into the solid solution area, GOSE'A (Fig. 217) (as already described in the annealing of a single phase) the material assumes a granular structure, thereby modifying the original form resulting on solidification; N. J. Bélaiew has termed this the "granulation area" (domaine de granulation).

(3) During the transformation in the solid state, the pro-eutectoid constituents, ferrite or cementite according to the carbon content, separate from the gamma iron—carbon solid solution assuming, in the case of a slow transformation, a cellular or network structure, and with more rapid transformation the Widmanstaetten structure. The microstructure of cast steel is therefore characterised by two limiting structures, and as a general rule both forms are present. Usually a network of ferrite or cementite is present outlining the pearlite areas, which are crossed by plates or needles of ferrite or cementite. This structure, easily visible under low magnification, is one of the causes of weakness in cast material; it must be destroyed for the same reason that it is desirable to avoid a large or coarse structure; hence the annealing operation to which cast material is subjected (Figs. 274–277, Pl. XLVIII., p. 144).

1B. **Steel that has been Forged, Rolled or Stamped but not Quenched.**—In these steels, the dendritic structure of primary solidification, revealed by macroscopic examination, has been partially destroyed by mechanical treatment; macroscopic examination will therefore show a fibrous structure, the fibres being in the direction in which elongation has taken place. This subject will be more fully considered under Macrostructure (see Chap. VI.). Microscopical examination shows the primary crystalline arrangement and distribution of the constituents to have been destroyed, and in many instances there will be seen a regular distribution of the constituents, ferrite-pearlite or cementite-pearlite, of no definite shape; however, two forms of distribution should be noted, A and B, the first of which is characteristic of products that have been submitted to mechanical treatment.

A. **Banded or Striped Structure.**—(Figs. 279, 280, 281, Pl. XLIX., p. 144.)—If a longitudinal section of a rolled or forged bar of hypo-eutectoid steel is examined, it will frequently be found that the ferrite and pearlite are distributed in bands giving the structure a striped appearance. It should be observed that if there are any visible inclusions, especially sulphide of manganese, these inclusions are contained in the ferrite bands, hence the hypothesis already mentioned (mainly supported by Ziegler and Brearley), of the part taken by these

inclusions as an agent in the separation of the pro-eutectoid constituent. This "banded distribution" of the constituents must be distinguished from the simple elongation of the ferrite and pearlite produced by simple pulling out in one direction (Figs. 282–284, Pl. L.). This banded structure is accentuated by annealing. It may also be found in hyper-eutectoid steels (Figs. 225–226, Pl. XXXV.).

B. **Widmanstaetten Structure.**—If a piece of steel is retained for a long period at a high temperature within the solid solution area (granulation zone, Bélaiew), growth of the crystal grains occurs in accordance with the general law, the amount of growth increasing with the temperature and the time heated. Since forged articles are usually allowed to cool in air, there is always a tendency for the intragranular separation of the pro-eutectoid constituent, corresponding to the formation of the Widmanstaetten structure. This may frequently be observed in articles in the forged condition, as already stated by Bernard and one of the authors,[1] the structure being visible at comparatively low magnifications (Fig. 278, Pl. XLIX., p. 144). In this condition the material possesses a very low impact figure, but subsequent annealing reduces the brittleness of the material by destroying this structure.

As a general rule, the texture or structure will be finer the lower the temperature at the finish of the mechanical treatment. If this temperature is higher than the temperature for the separation of the ferrite, the ferrite grains of that phase will be more or less equiaxed; on the other hand, after cold work they will be elongated in the direction of working.

In the case of steel which is annealed as a final treatment, the grain size (the grain size of the solid solution defining the grain size after transformation on cooling) will increase and become of greater importance as the annealing temperature, the annealing time, and the carbon content increase.

Special Cases—Tendency towards Structural Equilibrium of the Ferrite-Cementite.—It has been shown that, as a general rule, heating an alloy in an area consisting of two phases tends to bring about grain growth, due to the coalescence of the respective particles of each phase and a consequent decrease in the number of particles. Further, in the case of the formation of one or two phases, the particles of these phases will be larger the slower the rate of formation. The combined effect of these two actions will tend to coarsen the structure of the lamellar eutectoid conglomerate of ferrite-cementite and to transform the structure into rounded masses (compare

[1] Portevin and Bernard, *Revue de Met.*, vol. ix. p. 544, 1912. However, when the primary network is partially due to the inclusions, it persists even after heat treatment and the material remains brittle (Portevin and Bernard, *Revue de Met.*, vol. xii. p. 155, 1915).

Figs. 268, 269, Pl. XLVI., with Figs. 270, 271, Pl. XLVII., p. 144), giving in the first instance granular pearlite and finally bringing about the isolation of massive ferrite and cementite. The estimation of the carbon content from the amount of pearlite present is thus rendered inaccurate and therefore impracticable. In practice the effects of these phenomena are found in the following instances :—

A. *Blister Steels.*—These are steels obtained by the complete cementation of wrought-iron bars ; owing to the method of manufacture, the operation occupies several weeks and the cooling is exceptionally slow. Microscopical examination shows the steel to consist of separate portions of ferrite and cementite, or of lamellæ of cementite, ferrite, and pearlite which are visible under the lowest magnifications (×50).

B. *Granular Pearlite.*—Granular pearlite is obtained by prolonged annealing of pearlite, about 700° C., or by slowly passing through the pearlite formation temperature.[1] It may also be formed by the annealing operations to which bars and wires are subjected during drawing operations.

C. In *Damascus steel,* the structure of which is obtained by very slow cooling, the cementite exists in the granular condition (Belaiew).

2. **Steels, Quenched or Quenched and Tempered.**—The character of the various constituents will be chiefly considered. Quenching is said to be the more severe the more it lowers the transformation zone on cooling, and therefore the more it tends to retain the condition of the material that is stable at high temperatures or the transitional constituent most nearly approaching this condition. As a general rule, the quenching is more severe the higher the temperature and the more rapid the cooling ; the rate of cooling is dependent, as previously mentioned, on the conductivity of the bath, the quenching temperature, the size of the article, and the shape of the section of the article that requires quenching.

With iron-carbon alloys, the retention of the stable condition at high temperature is facilitated not only by greater severity of quenching, but also by increasing carbon content (also by other elements such as manganese and nickel). If these conditions are considered in conjunction with the general quenching conditions mentioned in Chap. II., the following conclusions are arrived at :—

1. Austenite will only be obtained by severe quenching of steel of high carbon content. Thus the maximum amount of austenite was obtained by Osmond on quenching small specimens containing 1·6 per cent. C from a high temperature in ice-cold water. It has not yet been obtained in the pure condition in simple Fe-C alloys ;

[1] For examples, *see* Portevin and Bernard, *Revue de Met.*, vol. xii. p. 161, 1915.

EFFECT OF THE RATE OF COOLING ON THE CONSTITUTION OF STEELS.

Micrographs of a specimen of 0·4 % C. steel heated and quenched at one end, showing the gradual change from martensite to ferrite-pearlite.

Etchant: Picric acid.
(× 200.)

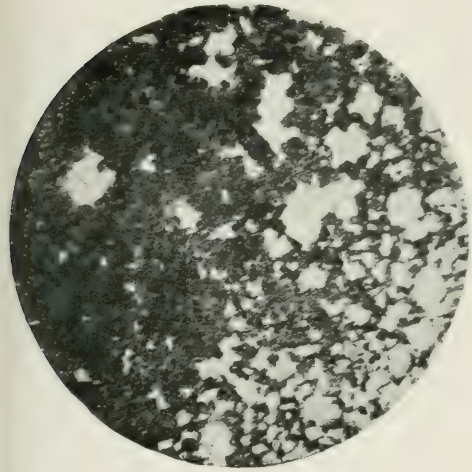


FIG. 286.—Heated end. Martensite-troostite.

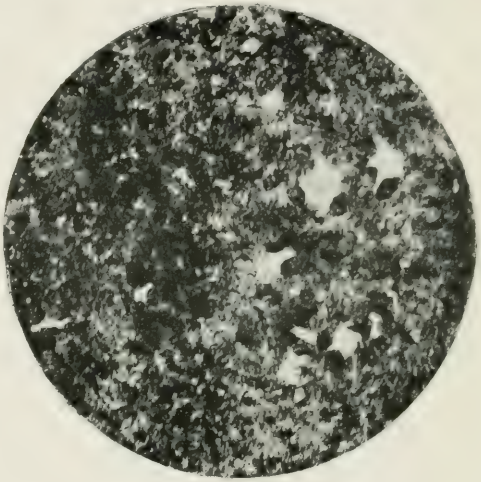


FIG. 287.

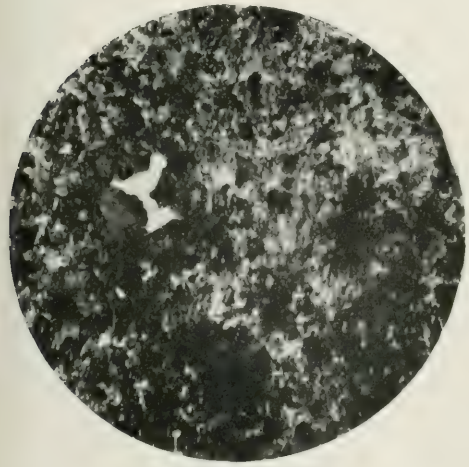


FIG. 288.

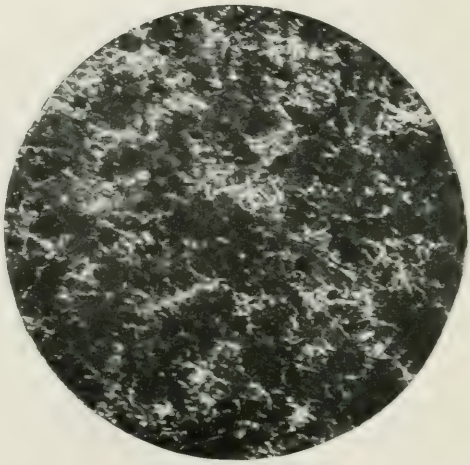


FIG. 289.

EFFECT OF THE RATE OF COOLING ON THE CONSTITUTION OF STEELS (*cont.*).

Micrographs of a specimen of 0·4 % C. steel heated and quenched at one end, showing the gradual change from martensite to ferrite-pearlite.

Etchant: Picric acid.
(× 200.)

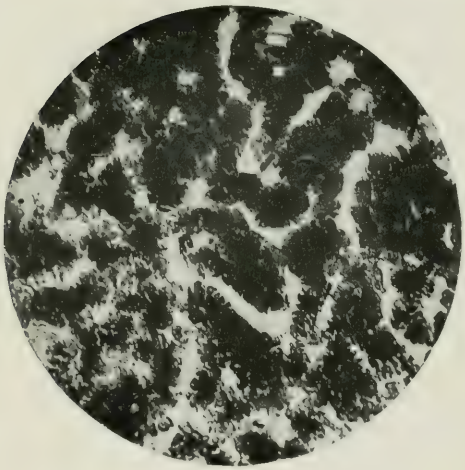


Fig. 290.

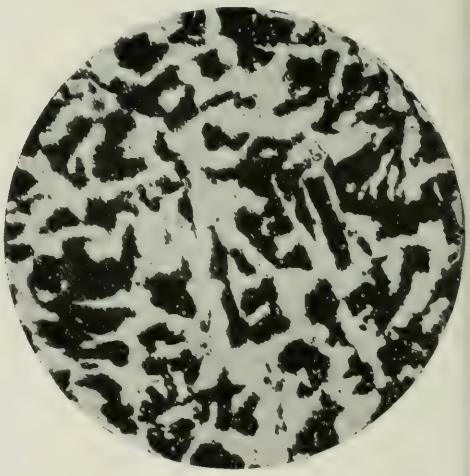


Fig. 291.

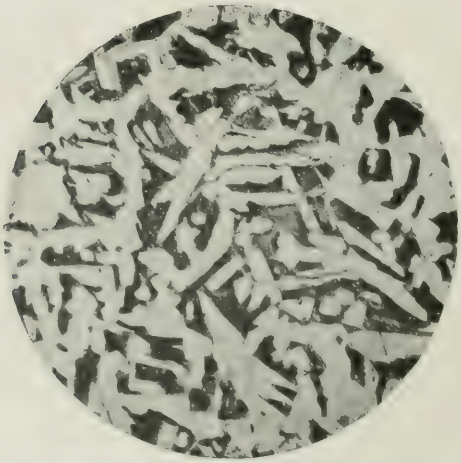


Fig. 292. Unheated end. Ferrite-pearlite.

WHITE CAST IRONS.

FIG. 293.—Hypoeutectic white iron 3·6 % C. The dark pearlite appearing as primary dendrites in a white ground mass of eutectic. (× 10.)

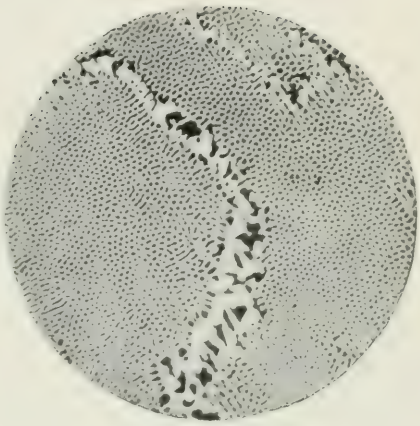
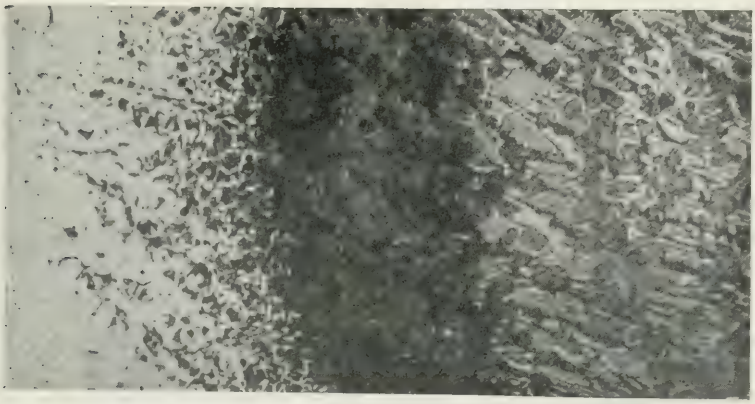


FIG. 294.—Eutectic white iron. Etchant: Picric acid. (× 200.)

Iron cemented in liquid cast iron.

Etchant: Picric acid



Ferrite. Ferrite and pearlite. Pearlite. Pearlite, white iron eutectic and cementite.

FIG. 295.

CONSTITUENTS OF THE IRON-CARBON ALLOYS—WHITE CAST IRON.

1° Hypoeutectic cast iron.
(× 200.)

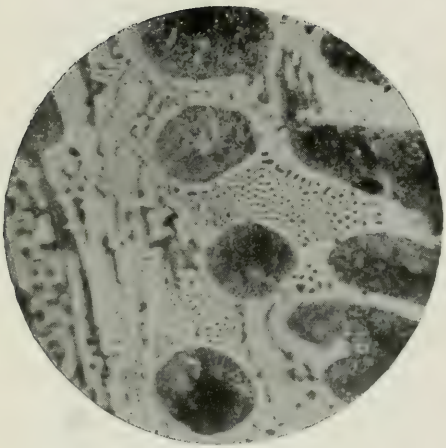


FIG. 296.
Etchant: Picric acid.

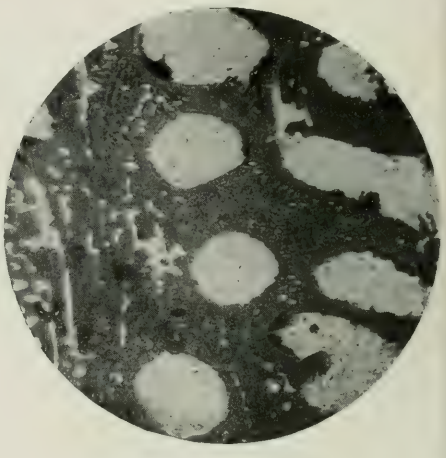


FIG. 297.—Same field.
Etchant: Sodium picrate.

2° Hypereutectic cast iron.
(× 200.)

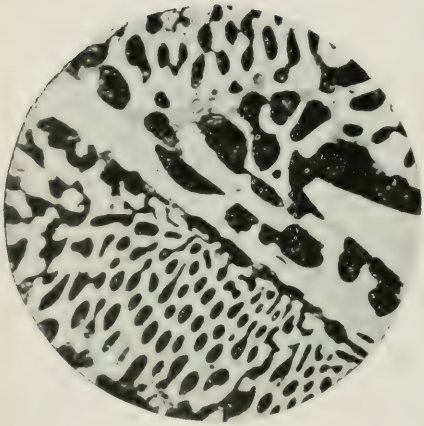


FIG. 298.
Etchant: Picric acid.

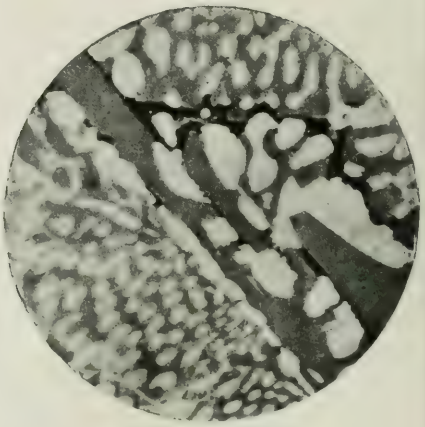


FIG. 299.—Same field.
Etchant: Sodium picrate.
(Traces of phosphide eutectic have etched black.)

HYPEREUTECTIC WHITE IRONS.

Etchant: Picric acid.

The primary cementite appears as white needles.
The pearlite of the eutectic etches dark.

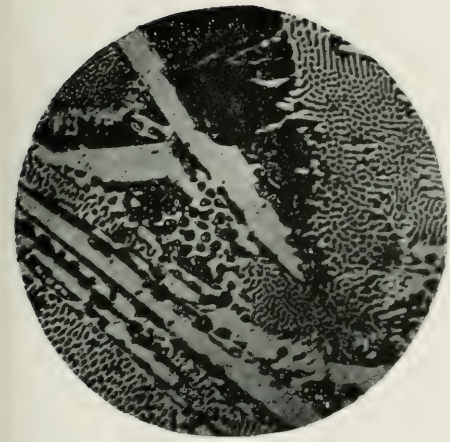


FIG. 300.
(× 200.)

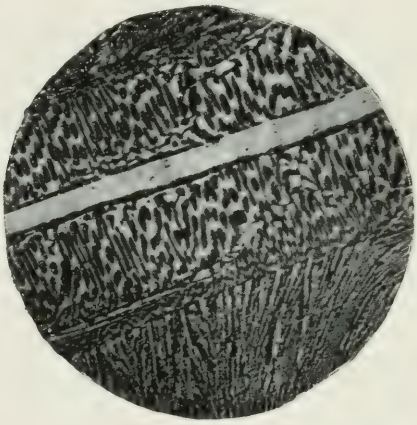


FIG. 301.
(× 200.)

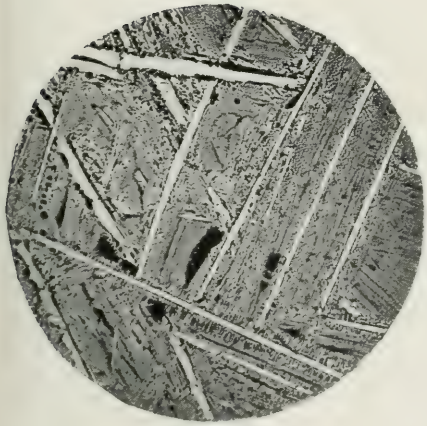


FIG. 302.
(× 50.)

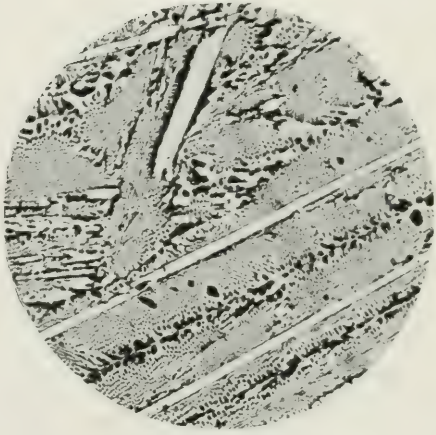


FIG. 303.—C = 4·0 %; Si = 0·35 %; Mn = 4·0 %.
(× 200.)

GREY CAST IRON.

The same field etched with various reagents.
(× 207.)

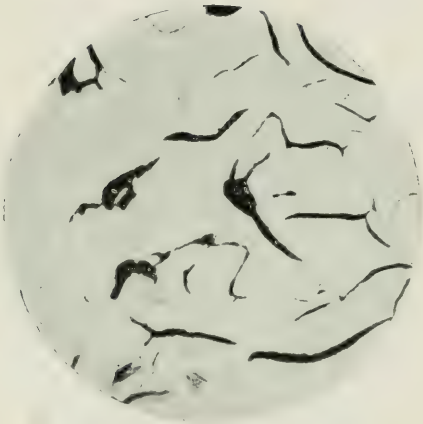


Fig. 304.—As polished.
Graphite black.

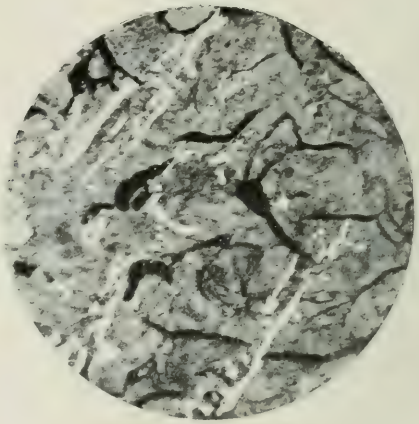


Fig. 305.—Etchant: Picric acid.
Graphite, black.—Pearlite, grey.
Cementite, white.

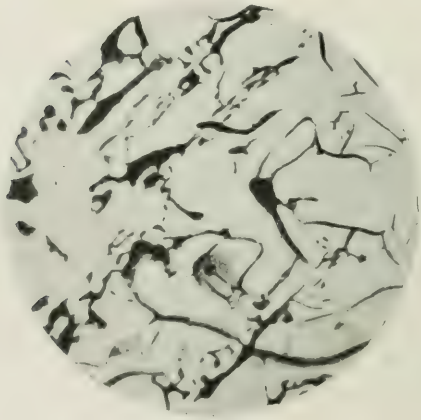


Fig. 306.—Etchant: Sodium picrate.
Graphite and cementite, black.

CAST IRONS.

1° Mottled iron.

The same field etched with two different reagents.
(× 200.)

FIG. 307.—Etchant: Picric acid.

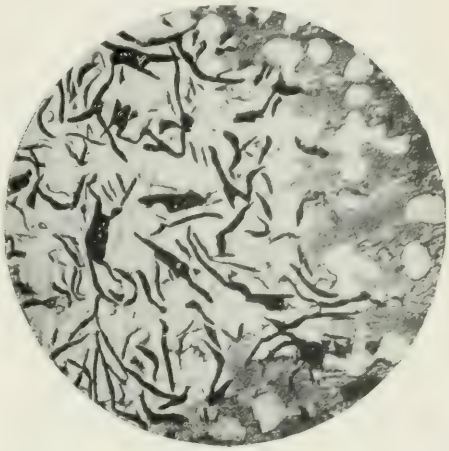


FIG. 308.—Etchant: Sodium picrate.

2° Nickel cast iron (Ni = 5·88; C = 1·69).

FIG. 309.—Etchant: Picric acid.

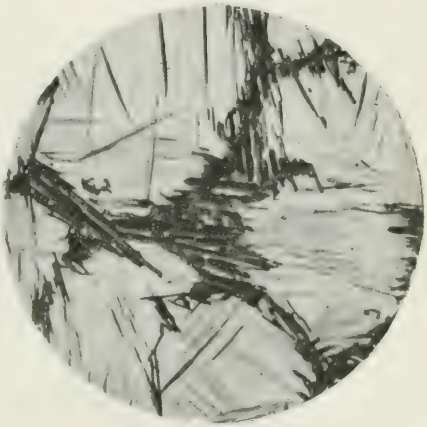


FIG. 310.—Etchant: Sodium picrate.

PHOSPHORIC WHITE IRONS.

Same field after various etchings.

(× 200.)

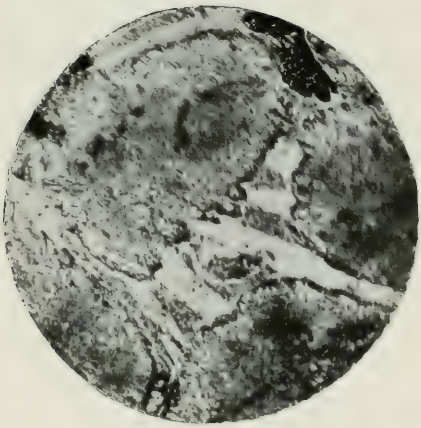


Fig. 311.—Etchant: Picric acid.

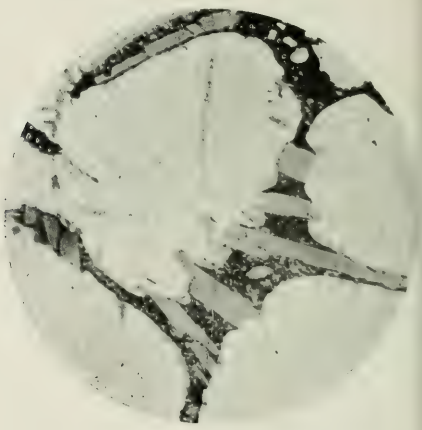


Fig. 312.—Etchant: Sodium picrate.

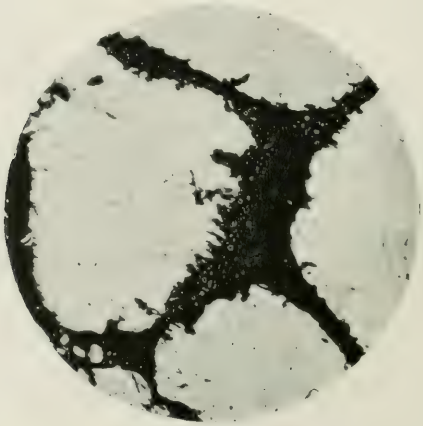


Fig. 313.—Prolonged etching in sodium picrate.

the addition of 2·2 per cent. Mn has enabled Maurer to obtain pure austenite on quenching in water from 1050° C.

2. Pure martensite will only be obtained by quenching above the line GOSL; quenching below will result in the formation of ferrite-martensite or cementite-martensite with, in most cases, some troostite at the boundaries of the two constituents. A similar result is obtained by insufficient heating before quenching.

In the case of low carbon steels pure martensite will only be obtained by severe quenching. Except in the case of small specimens, quenching will only give a surface layer of pure martensite; on passing from the outside to the interior of the specimen there will be found increasing quantities of troostite together with ferrite in the hypo-eutectoid steels, or cementite in the hyper-eutectoid steels.

3. Quenching near the Ar_1 point produces troostite. The same result is obtained by quenching in oil, warm water, etc.

4. The austenite-martensite structures obtained by severe quenching possess a characteristic structure, the martensite appearing as needles, arrowheads, zigzags, etc., in a background of austenite; when the proportion of austenite present is small, a thickening and general growth of the martensite needles occurs and they are then more clearly visible; the martensite is said to have a coarse structure.

Distribution of the Constituents produced by quenching.—This subject can only be briefly considered.

1. The arrangement of the martensite needles corresponds with the cleavage planes of the austenite from which they are formed.

2. If martensite and cementite are both present, the latter may appear, as thin filaments, as the remains of the cellular network, as needles, or even as small rounded or granular particles; it is generally surrounded by troostite; under certain conditions, when all the cementite has disappeared through quenching, the troostite may, within certain limits, have a similar distribution. But more frequently troostite exists as small rounded masses having in their centres either cementite, ferrite, or martensite.

3. Troostite, being formed by the transformation of martensite, will naturally at first assume the same form as the latter, appearing as needles, spear-points, etc.; it is more easily attacked by reagents. Kourbatoff has termed this troosto-sorbite.

Tempering.—Tempering is a method of causing the transformation to occur at a slow speed, the various transitional constituents being produced in the following order, the pro-eutectoid constituents, ferrite or cementite, being liberated at the same time:[1]

$$\text{austenite} \rightarrow \text{martensite} \rightarrow \overbrace{\text{troostite} \rightarrow \text{sorbite}}^{\text{osmondite}} \rightarrow \text{pearlite}$$

[1] The ferrite in this instance separates as extremely fine needles which accentuate the martensitic appearance.

Figs. 286–293, Pls. LI. and LII. (p. 152), show a series of typical structures; the sharp change between martensite and troostite will be observed. Frequently one of the intermediate stages in the return to the pearlitic state does not appear and there is the direct conversion :

austenite → troostite

Double quenching.—This term is employed in the case of two successive quenchings at different temperatures, the second quenching being at a lower temperature than the first. This form of treatment may be employed in the following instances :—

1. In homogeneous steel, in order to obtain sorbite in high carbon steels ; it may be considered to consist in quenching followed by tempering, the second quenching being made at a temperature between 300° and 700° C.

2. In homogeneous steels of coarse structure (ex. cast steel) the structure is refined by the first quenching, and this enables a fine structure and good mechanical properties to be obtained from the second quenching.

3. In case-hardened or cemented steel, with the object of increasing the strength and reducing the brittleness of the core. The result obtained by such treatment consists of a core of extremely fine grain or texture with a case of pure martensite.

B. **Cast Iron** (*see* Pl. LIII.–LVIII., p. 152)

Constituents.—Practically the only constituents to be met with in ordinary cast irons are : cementite, pearlite, graphite, and ferrite. The first two belong to the labile system Fe-Fe_3C, the last two to the stable system Fe-graphite. During solidification in the labile system, a eutectic is formed at 1130° C. consisting of Fe_3C-solid solution 1·7 per cent. C, the carbon content of the eutectic being 4·3 per cent. C (Fig. 295, Pl. LIII.) ; during the subsequent cooling, the proportion of cementite present increases owing to the separation of cementite along the line SE′ (Fig. 217, p. 129). This secondary deposition of cementite either unites with the existing eutectic cementite or remains isolated in the solid solution, forming the free pro-eutectoid cementite (cementite needles in Figs. 311 and 312, Pl. LVIII.) ; but this change has but little effect on the distribution of the eutectic constituents as regards the microstructure. Finally, the formation of the eutectoid pearlite occurs when the content of the solid solution has dropped to 0·9 per cent. C (point S on the diagram).

Since, in practice, these alloys are never quenched or chilled in the solid state, the quenched constituents which, in this case, take the place of pearlite, are rarely seen.

The term " chill " applied to cast irons is used in the case of

rapid solidification (casting in metal moulds—chill moulds) which produces the labile condition—white irons. This explains why elements such as manganese, which tend to produce white iron, facilitate the chilling effect.

Structure.—Cast irons undergo no mechanical treatment; their structure is that produced during solidification and subsequent transformations in the solid state. The types of structure will therefore be similar to those described in Chap. II.

1. **White Irons.**—In alloys containing less than 4·3 per cent. C, the solid solution, iron-carbon, separates from the liquid in the form of dendrites, easily visible at low magnifications (Fig. 294, Pl. LIII.); these dendrites are surrounded by eutectic, the structure of which is resolved at medium magnifications; at the higher magnification the sections through the branches of the dendrites appear as rounded or elongated masses (Figs. 296, 297, Pl. LIV.). The primary solid solution forming one of the constituents of the eutectic is replaced by pearlite or sorbite which may or may not be traversed by needles of pro-eutectoid cementite. The eutectic containing 4·3 per cent. C presents either a speckled (Fig. 294, Pl. LIII.) or a striped appearance, according to the orientation of the grains of eutectic in the section. In the alloys containing above 4·3 per cent. C, plates of primary cementite will be observed in a background of eutectic (Figs. 298, 299, Pl. LIV.; Figs. 300–303, Pl. LV.).

2. **Grey Cast Irons.**—After simple polishing, the graphite may be seen as: long black threads in the case of primary graphite separating from the liquid (Fig. 304, Pl. LVI.; Fig. 231, Pl. XXXVII.); as short threads or rounded particles if it is graphite formed by the decomposition, on annealing, of the cementite or the solid solution in a white iron (temper carbon). The distribution of the graphite-ferrite sometimes suggests the appearance of a eutectic, but the existence of such a eutectic is disputed.

As a general rule, graphite and ferrite are not the only two constituents present, and other constituents are found indicating a combination of the two systems of which graphite and cementite are the distinguishing features. There are usually present either graphite-ferrite-pearlite (the ferrite as a border round the graphite), or graphite-pearlite-cementite (Figs. 306–308, Pl. LVI.), or even all four constituents. The various constituents may be easily identified, graphite before etching (Fig. 304, Pl. LVI.; Figs. 231, 232, Pl XXXVII.), after etching with picric acid (pearlite coloured) (Fig. 305, Pl. LVI.; Fig. 309, Pl. LVII.), or picrate of soda (cementite coloured) (Fig. 308, Pl. LVI.; Figs. 308–310, Pl. LVII.).[1]

[1] The cast irons known as "semi-steels" are grey cast irons of low carbon content (3 per cent. mean); to possess good mechanical properties and to machine easily their structure should consist of fine graphite and pearlite, no ferrite and but little or no cementite.

In the phosphoric cast irons (Figs. 313–315, Pl. LVIII., p. 153) the presence of phosphide of iron will be noticed and may be identified from the description given under the heading of inclusions.

Case-hardened Steels and Malleable Cast Iron

The above are the products obtained by carburisation or decarburisation of iron-carbon alloys in the solid state. Consequently they are the products of an action which occurs at the surface of the material and the effect of which varies in depth, this being especially the case when the reaction has not been completed throughout the mass. Except in the latter case the product obtained will be heterogeneous and the carbon content of an outer layer of variable thickness alone will be affected. The result obtained may therefore be graphically represented by a curve in which the depths from the surface of the article treated are abscissæ and the carbon contents for each depth are ordinates; the relation between the distance from the surface and the carbon content is thereby obtained—"*concentration-depth diagram.*"

Case-hardened or Case-carburised Material

Case-hardening or case-carburising is defined as being a superficial carburisation of a steel of low carbon content by heating this steel in a medium, either solid, liquid, or gaseous, which will give up all or part of its carbon to the steel (the medium being termed a *cement*) at a temperature between the lower transformation temperature and the solidus of the steel treated. The process of case carburising is usually followed by quenching, but unquenched products will be considered in the present instance. Carburisation occurs from the surface and operates towards the interior; as already stated, there will be a gradual alteration of the carbon content in depth, and, as a general rule, at some given depth the carbon content will be that of the original steel. This depth is the limit of penetration and the distance from the surface is termed the thickness of the case. If the carbon content is at no point as low as the original carbon content, the case hardening is said to have penetrated to the core.

1. *In practice cementation is used for two purposes: complete cementation* of pure charcoal iron in order to obtain a pure iron-carbon alloy of high carbon content without the introduction of the impurities found in steels obtained by the more usual methods of production. This product (blister bar) is then melted in crucibles in the manufacture of crucible cast steel.

The study of the structure of blister steel is of doubtful importance. It may be noted that owing to the extremely slow rate of cooling,

the effects due to the coalescence of the cementite will usually be found (free cementite in a ground mass of ferrite or pearlite, the particles being easily visible under low magnifications). Microscopical examination enables some estimation of the carbon content to be made, but in practice the bars are sorted into stacks of definite ranges of carbon content by visual examination of the fracture.

2. *Surface carburisation or case hardening* is used in conjunction with subsequent quenching to give an extremely hard wearing surface to mild steels. As the depth of the case increases, the carbon content of the surface layer also increases and in many instances exceeds the eutectoid content of 0·9 per cent. C ; but it is possible to regulate the process in such a manner that the carbon content of the outer case will be less or greater than the eutectoid value or even 0·9 per cent. C.

Three distinct types of case are recognised (Giolitti) according to the carbon content of the surface:

Type I.—Hypereutectoid zone—cementite.
Type II.—Hypoeutectoid zone—ferrite.
Intermediate Type.—Eutectoid—pearlite.

The correct conditions to obtain one or other of these types of case are dependent on many factors, notably the nature of the cement and the cementation temperature.[1]

Type I. form of case is produced by the hydrocarbons and solid cements used at high temperatures. The use of pure carbon monoxide as a cement produces a case similar to Type II., whilst the intermediate type is produced by mixed cements such as powdered wood charcoal and carbon monoxide combined.

The formation of cementite is assisted by fluctuations in the temperature, as shown by Giolitti and Scaria, even when these fluctuations occur entirely above the separation temperature of pro-eutectoid cementite.

The microscopical examination of the unquenched case enables the carbon content to be estimated, and also permits the depth of the case and the variation of the carbon content in depth to be examined. This variation in depth may be gradual, but in some cases it is marked by very rapid changes.

These rapid variations commence, according to Giolitti and Tavanti, during slow cooling or passing through the initial separation temperature of the pro-eutectoid constituents—ferrite and cementite of the cemented case. The first particles of these constituents to separate act as nuclei, accumulating the ferrite and cementite subsequently separating from the solid solution, and thus tend to produce a rapid variation of the carbon content in depth.

[1] *See* Giolitti, "The Cementation of Steel." Portevin, "La cémentation par les céments mixtes" (*Bull. Soc. Ing. civils.*, October, 1913).

It is owing to this effect that, in cementations of Type I., there will be found a zone of pure pearlite of definite thickness separating the hypereutectoid and hypoeutectoid layers. Rapid changes of carbon content are always found in this type of case produced by a special class of cement known as "quick or rapid cements." [1] This rapid change in carbon content has been shown, by Giolitti and Tavanti, to be the principal cause of the flaking, chipping, cracking or breaking away of the case. The case breaks away in a manner very similar to that of a badly welded surface layer—in the form of plates and scales when the article is subjected to a repeated hammering action. Moreover, the presence of cementite on the outside of the case increases the brittleness and facilitates chipping, especially at sharp angles and corners of the article treated. Cementite needles (Widmanstaetten structure) are a particularly harmful structure, as this needle-like structure is due to the intersection, in the plane of the polished surface, of plates of cementite, which act as planes of weakness in the resistance of the material to impact. Their effect is more pronounced at corners and sharp angles, and their absence is therefore more important in these positions.

The microscopical examination of an ordinary steel, case-hardened and unquenched (Fig. 314, Pl. LIX.), provides much valuable information. As a general rule, the best results will be obtained with a case the outside carbon content of which is approximately 0·9 per cent. C, or only slightly exceeds this value, and has a regular decrease in carbon content in depth.

The 0·9 per cent. carbon content should be maintained to a certain definite depth in order that the hard case obtained by quenching may be of sufficient depth. The necessary grinding to finished dimensions after quenching must also be allowed for in the original depth of the case.

Microscopical examination after quenching also gives much valuable information (Fig. 315, Pl. LX.). As previously stated, in most cases the case, if it is to possess the maximum hardness, should consist of pure martensite containing 0·9 per cent. C. The presence of cementite after quenching renders the case very brittle and fragile; the presence of osmondite indicates too mild a quenching and in some instances too low a surface carbon content, which is verified by examination of an unquenched section. A low carbon content may be due to insufficient cementation or to decarburisation subsequent to cementation (during subsequent heating, etc.); in either case, microscopical examination of the annealed specimen

[1] The same authors have mentioned a further cause for the rapid variation of the carbon content in depth—cementation at too low a temperature (below the A_3 point). This cause is not met with in commercial manufacture under correct working conditions.

CASE HARDENED MILD STEEL (UNQUENCHED).

Fig. 314.—Cemented mild steel, unquenched.
Etchant: Bénédicks' reagent (1′ 30″). (× 180.)

CASE HARDENED STEEL (QUENCHED).

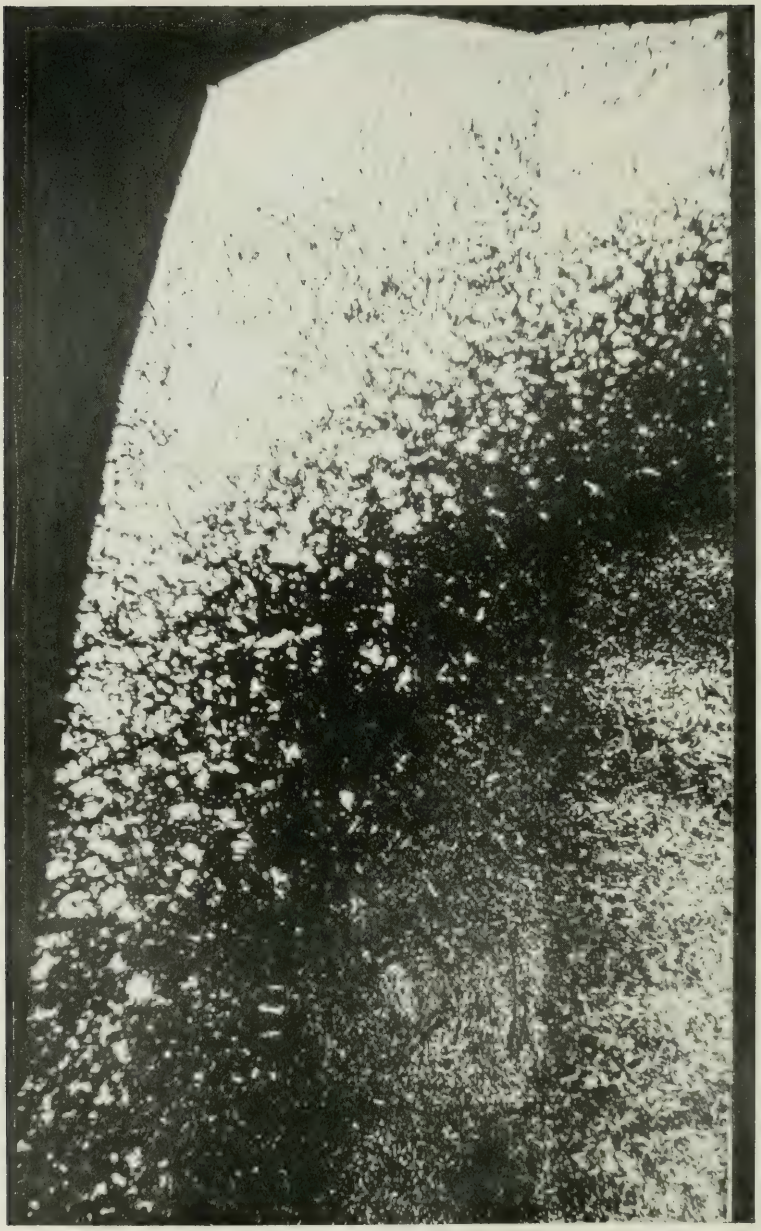


FIG. 315.—Section of tooth of a gear wheel, case hardened and quenched. On the edge white martensite, towards the interior troostite dark and ferrite white.

(× 75.)

will supply the information. Precautions must be taken in annealing to ensure that decarburisation does not occur—rapid annealing in a lead bath.

It must not be overlooked that, as stated by Berjot and one of the authors,[1] prolonged annealing completely alters the depth of the case and the distribution of the carbon. The cementation becomes progressively more uniform on continued heating at a high temperature. This method therefore offers a means of destroying the hypereutectoid surface when this exists, but at the same time it alters the depth of the case.

In commercial practice the thickness of the case is estimated from the fracture of the quenched case-hardened specimen. Under these conditions a very definite dividing line between the case and the core is seen by the rapid change in fracture,[2] the case having a dull fine fracture, the core a coarser and brighter fracture. It is accepted that this sharp change in structure marks the limits of the core that can be estimated in this manner, but, as already stated by Berjot and one of the authors,[3] distinctly different results may be obtained from the microscopical examination of unquenched polished specimens after etching as compared with the estimation of similar specimens quenched and fractured. In the latter case the thickness varies according to the quenching temperature.

With hypereutectoid cases of high carbon content, the hypereutectoid section appears in the fracture as a series of facets similar in appearance to a white iron fracture in miniature. The fracture in this case shows three distinct areas.

Cementation of Special Steels.—The progressive changes caused by cementation (increase of the carbon content) will be shown by variations in structure in accordance with the diagrams given later (p. 173, *cont.*). It is merely necessary to consider the horizontal line corresponding to a given content of the special element in the steel in order to consider the various modifications occurring with an increase of the carbon content. Thus, commencing with a pearlitic nickel steel, it is possible to obtain by carburisation, and without quenching, a surface layer of martensite of extreme hardness [4]; or by commencing with a martensitic steel, it is possible by cementation to obtain an austenitic surface layer of less hardness (Mohs' scale).

The *speed of penetration* which is defined as the thickness of case produced by cementation for a definite time at a definite temperature is altered by the presence of certain special elements, and is also dependent on the nature of the cement employed; thus

[1] Portevin and Berjot, *Revue de Met.*, vol. vii. p. 74, 1910.
[2] When the case is not very deep.
[3] Portevin and Berjot, *Revue de Met.*, vol. vii. p. 73, 1910.
[4] Guillet, *Bull. Soc. Ing. civils*, fev. 1904.

nickel has been stated to both increase (Guillet) and decrease (Giolitti) the rate of cementation according to whether the Caron cement (charcoal+barium carbonate) or the mixed cement (C+CO) is employed.

Cementation of chrome, tungsten, molybdenum, and vanadium steels of low carbon content brings about the formation of the double carbides.[1]

Steels containing 2 per cent. or more of silicon and aluminium are not cemented by wood charcoal.

Malleable Cast Iron

Malleable cast iron is manufactured by submitting cast iron containing approximately 3 per cent. C and fairly low manganese to prolonged annealing at 1100° C. in some oxidising medium. Three changes will be observed to occur:

1. Progressive decarburisation from the surface inwards which may be complete in the case of thin articles.

2. Precipitation of graphite and the establishment of stable equilibrium in the central portions of thicker articles.

3. General grain growth of the constituents, produced by the prolonged heating at high temperature. The resulting weakness and brittleness may be destroyed by a second annealing or, better, by air quenching.

These three phenomena having been previously considered and described, the present description will be confined to their application.

Finally, cast iron is sometimes rendered malleable (American method) by simple annealing, without oxidation, decomposing the cementite with the formation of temper carbon.

Connection between the Mechanical Properties, the Equilibrium Diagram, and the Treatment

Connection between the Mechanical Properties and the Diagram.—The diagram shows the constitution of annealed iron carbon alloys at ordinary temperature. The relation between the constitution and mechanical properties will now be considered.

The iron-carbon alloys consist of ferrite—pure iron (malleable, ductile, soft)—and cementite—carbide of iron (definite compound, hard, brittle); these two constituents are present partially intermixed in the form of a fine conglomerate, pearlite. The percentage proportion of ferrite (total ferrite) decreases, and the percentage proportion of cementite (total cementite) increases proportionally

[1] Guillet, *Bull. Soc. Ing. civils.* fev. 1904.

with the carbon content as indicated in diagram, Fig. 316 (Howe). The ductility decreases proportionally as the amount of ferrite is reduced, whilst the hardness increases with the proportion of cementite present. As regards the ultimate strength, this increases up to 1·25 per cent. C, then commences to decrease, the free cementite then affecting and decreasing the strength of the pearlite structure in which it is intermixed.

The diagram therefore represents the variations of the principal

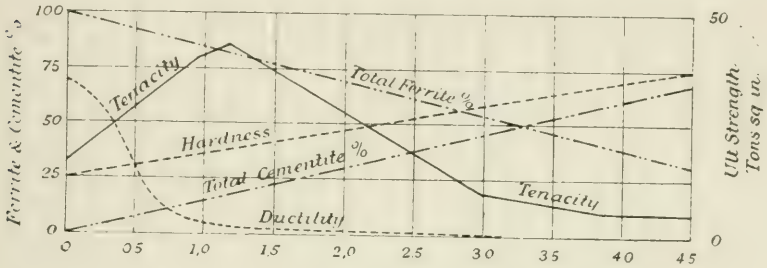


FIG. 316.

statical mechanical properties with alteration of carbon content. As regards the brittleness and resistance to impact, this property depends not only on the proportion of the constituents present, but also on their relative distribution and size, including grain size. It is therefore impossible to illustrate this property as a function of the chemical composition of the alloy, but, other conditions being equal, its value also diminishes in proportion to the free cementite present.

Annealed Steels.—With annealed steels it is possible to define

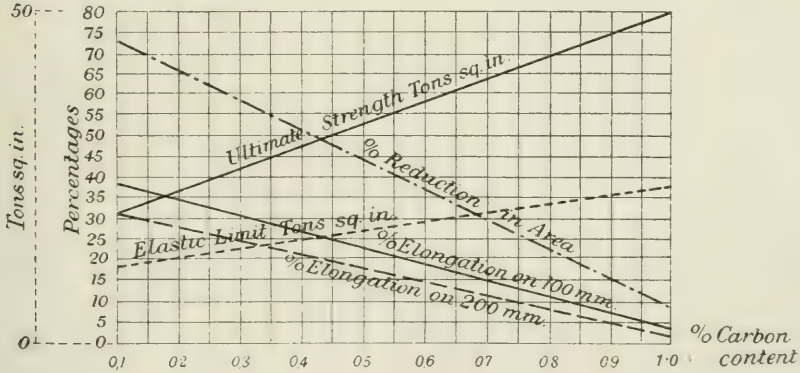


FIG. 317.

the static mechanical properties as a function of the carbon content by means of Deshayes' diagram (Fig. 317), plotted for pure steels and applicable to steels of varying chemical composition by employing one of the many formulæ for calculating the ultimate strength and percentage elongation for varying chemical composition.

The following examples may be quoted :—

Deshayes—

$$R = 30 + 18C + 36C^2 + 18Mn + 10Si + 15P$$

$$\text{elongation per cent.} = 42 - 36C - 5{\cdot}5Mn - 6Si$$

The equations formulated by Osmond distinguish between open hearth and Bessemer steels—[1]

$R = 26 + 60C + 23Mn + 11Si + 65P$ (35–60 ton Bessemer steel)

$R = 26 + 46{\cdot}5 + 21Mn + 11Si + 65P$ (22–40 ton Marten steel)

Juptner's equation—

$$R = 25 + \frac{200}{3}C + \frac{200}{7}Si + \frac{100}{7}Mn$$

Alloys containing Graphite.—In grey cast iron the graphite, which is soft, friable, and porous, tends to decrease the hardness and the

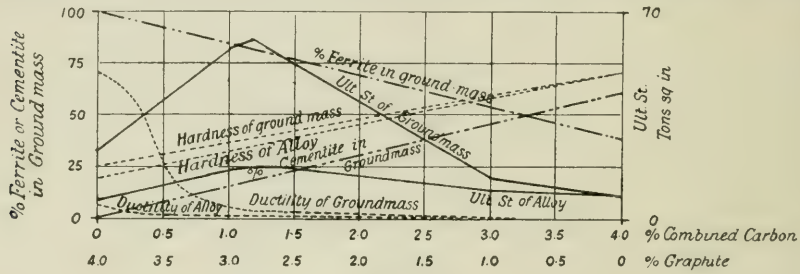


FIG. 318.

ultimate strength and to increase the porosity of the metal ; further, it lessens the ductility by causing discontinuity in the metal. Thus the mechanical properties of a cast iron are inferior to those of an alloy in which the graphite is absent but which is of otherwise similar composition.

If a series of alloys of the same *total* carbon content, *e.g.* 4 per cent. C, are examined, the greater the amount of free graphite the less the amount of carbon in the ground mass surrounding the graphite flakes ; but the properties of the ground mass are given by the diagram, Fig. 316. The properties of an alloy containing 4 per cent. C may therefore be deduced as a function of the graphite content as illustrated in the diagram, Fig. 318 (Howe).

The proportion of graphite for a given total carbon content depends, as already mentioned, on the rate of cooling and the manganese and silicon contents.

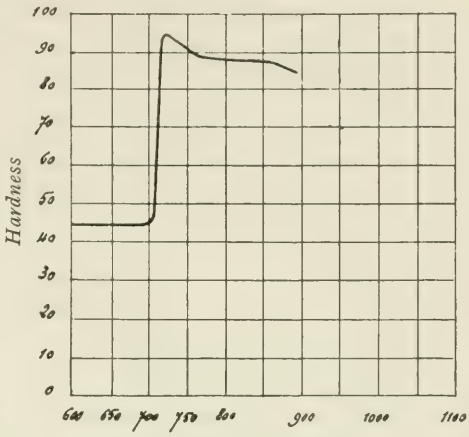
Connection between the Mechanical Properties and the Treatment of the Material (Steel)

Only the main outlines of this subject, which has been the object of many researches, can be dealt with in the present instance.

[1] Translator's note : The ultimate strength = R will be given in kilos m/m_2. To convert to tons sq. in. multiply this result by 0·631.

It will be remembered that for any given carbon content martensite is the hardest constituent of steels, harder, more particularly, than austenite and troostite. Troostite is harder than sorbite and pearlite. Inversely, martensite is, as a general rule, very brittle, and sorbite possesses the greatest resistance to shock or impact.

These data will explain the general results which follow :—



Quenching Temperature.

FIG. 319.

1. **Effect of Quenching Temperature.**—A steel containing approximately 0·9 per cent. C, and consisting entirely of pearlite, may be taken to illustrate the changes in a definite mechanical property, such as hardness, produced by variations in the quenching temperature. The variations of the scleroscope hardness give a curve of the form Fig. 319 (Portevin and Berjot) ; on passing through the transformation point the formation

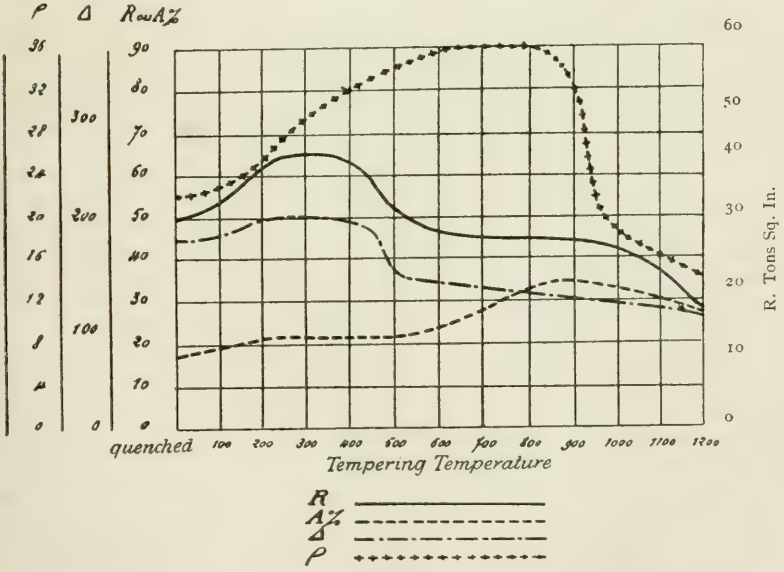


FIG. 320.

of martensite is marked by an enormous increase in hardness.[1] As the quenching temperature increases, the retention of austenite in increasing amount causes a slow diminution of the hardness.

[1] See also McCance : *Jour. I. and S. Inst.*, vol. lxxxix. pp. 192–244, 1914.

2. Effect of the Tempering Temperature.—The effects produced by varying tempering temperatures will be illustrated by means of three diagrams, Figs. 320, 321, 322, produced by Grard from results obtained with a mild steel (ult. st. 28 tons sq. in. in the annealed state), a medium carbon steel (ult. st. = 38 tons sq. in. annealed), and a hard steel (ult. st. = 45 tons annealed). The tempering

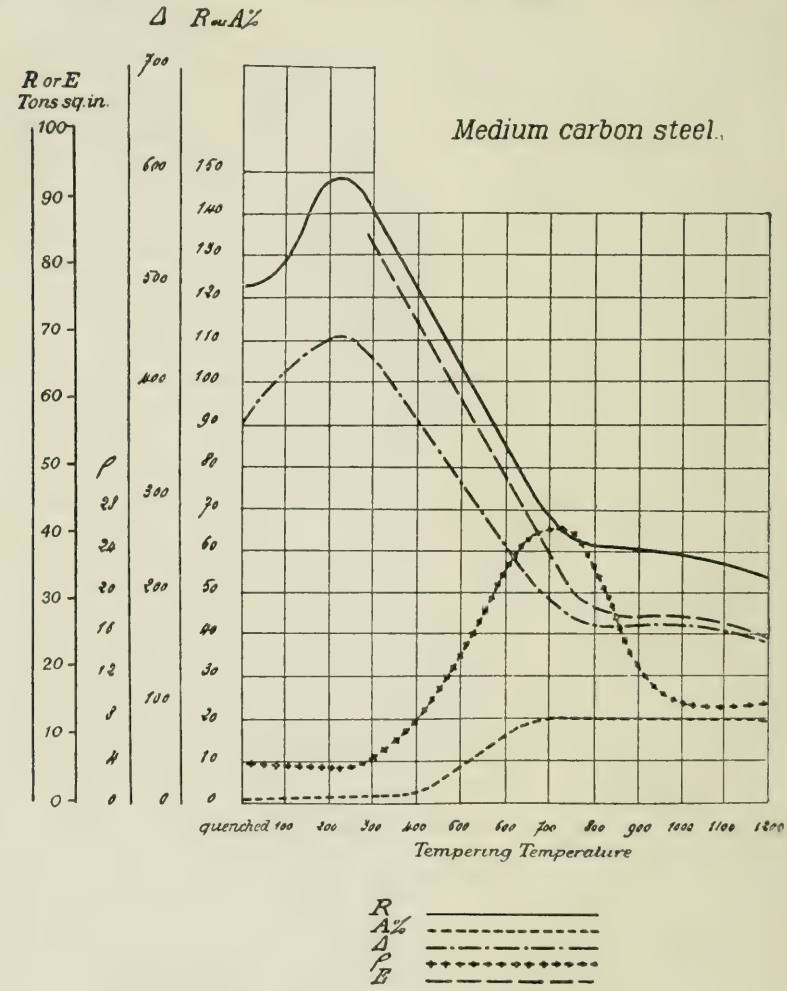


FIG. 321.

temperatures after quenching are plotted as abscissæ, the varying values of the different mechanical properties as ordinates.

Particularly to be noticed are—

1. The increase in hardness and ultimate strength on tempering at the lower temperatures, owing to the transformation of the residual austenite to martensite.

2. Above 200° C., the decrease in hardness, elastic limit, and

ultimate strength, and the increase in percentage elongation owing to the progressive transformation of martensite into troostite, sorbite, and pearlite.

3. The maximum impact figures obtained on tempering about 700° C., characteristic of sorbite.

4. The inclusion of re-heatings above 700° C. which constitute

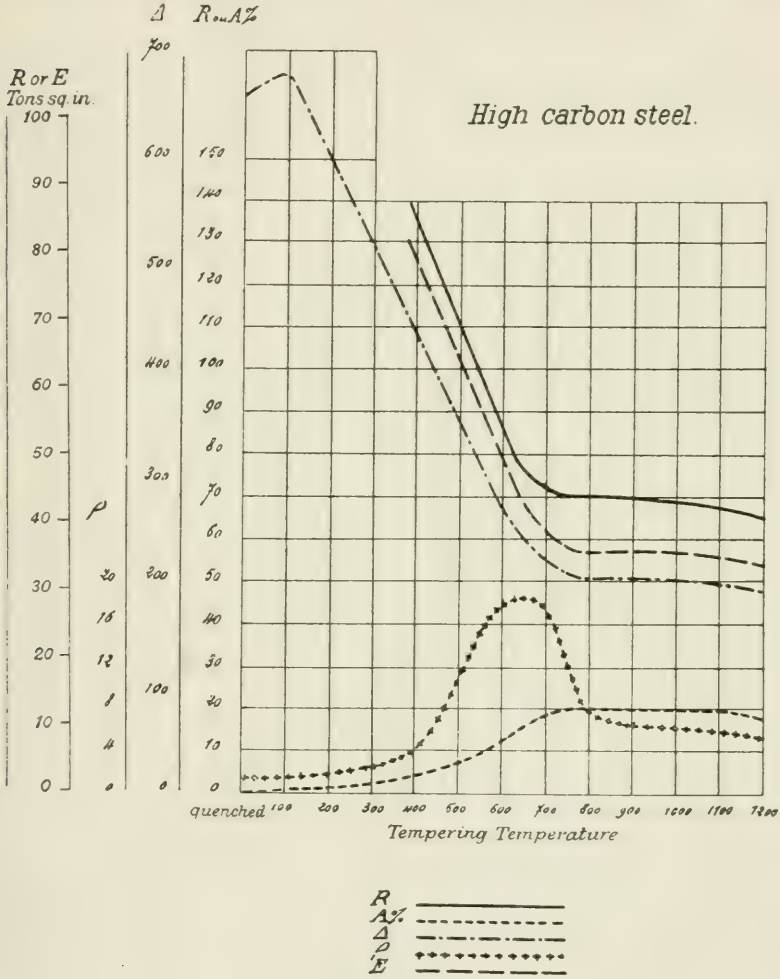


FIG. 322.

annealing operations. Under these conditions all the values of the mechanical properties are reduced by the consequent growth in grain size.

Connection between the Microstructure and the Fracture of the Material.—It is known that in tensile tests, fractures of various forms are produced; a definite connection exists between these fractures and the micro-structure of the material (Bannister)—

1. Cupped fracture: homogeneous steels of fine grain, no inclusions.

2. Lamellar or oblique fracture: distribution of the ferrite and the inclusions (MnS) in the form of bands (ghost lines).

3. Irregular fracture: irregular distribution of the ferrite, pearlite, and inclusions.

SPECIAL STEELS

Methods of Classification.—As previously stated, special steels and cast irons are those iron-carbon alloys to which definite quantities of some special element or elements, such as nickel, manganese, silicon, chromium, tungsten, vanadium, . . ., have been intentionally added. They are, essentially, at least ternary alloys Fe—C—M. Their logical method of examination would be by means of equilibrium diagrams, but to the complexity of such diagrams is added the additional complication that most of these special elements introduce important hysteresis effects which render it practically impossible to establish perfect physico-chemical equilibrium conditions. Therefore but few limited attempts have been made in the construction of such diagrams.

If, on the contrary, a definite transformation of an iron-carbon alloy of definite constant carbon content is considered, the addition of one of the special element will have a double effect [1]:

1. Displaces the equilibrium transformation temperature.

2. Modifies the hysteresis effect.

These two causes operate simultaneously in modifying the transformation points on heating and cooling. Since the determination of the equilibrium temperature is either extremely difficult or impossible, it is necessary to study the hysteresis effect produced and the change in the transformation points on heating and cooling at definite rates of heating and cooling. Also, it has been shown, in the case of carbon steels, that the structure and properties of an alloy are dependent on the position of the transformation point at the time of cooling; this suggests the transformation point on cooling as the characteristic to be studied, and, in addition, the study of the hysteresis effect which permits an estimation to be made, within certain wide limits, of the displacement of this point with varying rates of cooling. There is thus a method of classifying the special steels and the effects produced by varying heat treatments. The structure, which is connected on the one hand with the previous

[1] Actually, the effect is even more complicated, the variance increasing by unity for each element added; thus the addition of a third element to a binary alloy splits up the eutectic solidification into two stages, the second stage only being at constant temperature (triple eutectic).

transformation during cooling, and also with the actual properties of the steel, may also serve as a basis of classification. Of these two methods of classification, the principles of which were suggested by Osmond, the classification according to structure is the more convenient to choose for the purposes of a work of this nature. However, the general outline of the classification according to the transformation on cooling will be described, the divisions and method of representation given being that adopted by Grenet.[1]

Classification of Steels according to the Transformation Temperatures on Cooling.—*Method of Representation.*—The transformations are represented by means of dilatation curves on heating (dotted line) and on cooling (continuous line).

For simplification, the several periods of transformation, which frequently are not individually discernible, are grouped as a single point. Each curve will therefore only have two changes of direction on heating and cooling, indicating the commencement and the end of the transformation. Below and above the period of transformation the curve shows the expansion of the steel in the stable condition at ordinary temperatures and the stable condition at high temperatures. The directions of these two portions of the curve are not greatly different. Fig. 326 represents such a curve: BC indicates the transformation on heating, EF that occurring on cooling; AB the stable condition, at ordinary temperature, on heating; CD the stable condition, at high temperatures, on heating; DE the stable condition, at high temperatures, on cooling; FA the stable condition, at ordinary temperatures, on cooling.

As previously mentioned, with a given steel the transformation temperature on cooling depends on: the maximum temperature attained, the length of time heated at that temperature, and the law of cooling.[2] For purposes of simplification, it will be assumed, in the following description, that the steels have been heated in equal periods of time to the same temperature (*e.g.* 900° C.), and the law of cooling will be defined as the mean rate of cooling within the area in which the transformation occurs, the following standard rates being adopted:—

Very slow cooling: 100° C. in 30 minutes.

Moderately slow cooling: approximately 100° C. in ten minutes.

Steels may, according to Grenet, be divided into four classes or groups.

[1] "Trempe, Recuit, Cémentation et conditions d'emploi des aciers," Paris, Béranger, 1911.

[2] The effect of the two factors, temperature to which the material is heated and the rate of cooling, has been more fully dealt with by one of the authors in the case of chrome-nickel steels (Portevin, *Revue de Met.*, Sept., 1917).

Group I.—Steels having approximately the same transformation temperature during slow cooling as on heating [1] (curve, Fig. 323).

Examples: Ordinary carbon steels and most of the special steels used commercially for structural purposes.

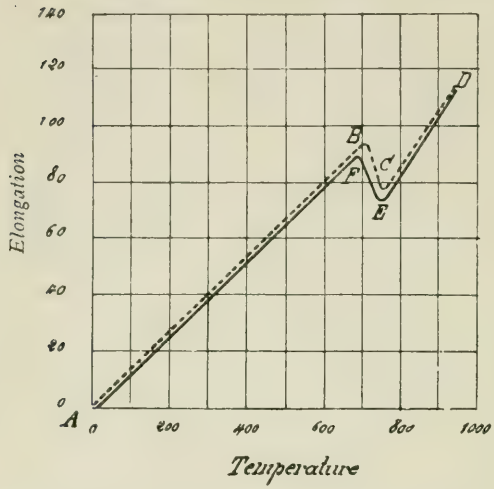


FIG. 323.—Group I. steels, actual cooling curves (Grenet).

Group II.—Steels having approximately the same transformation temperature during slow cooling as on heating (Fig. 324), but the transformation temperature of which at the medium rate of cooling is very much lower than on heating (curve, Fig. 325). The speed of cooling necessary to separate the two transformation temperatures is also dependent on the maximum temperature attained and the length of time this temperature has been maintained.

The high-speed tool steels may be mentioned as examples of this group (compositions, chrome-tungsten, chrome-molybdenum, chrome-tungsten-vanadium). With high-speed tool steels, the transformation on cooling may occur either between the transformation temperature and 600° C., or below 300° C., but not within a definite range between these two temperatures. Therefore under certain conditions of heating and cooling, the transformation on cooling is divided into two periods, a condition which may be found with all ordinary and special steels.

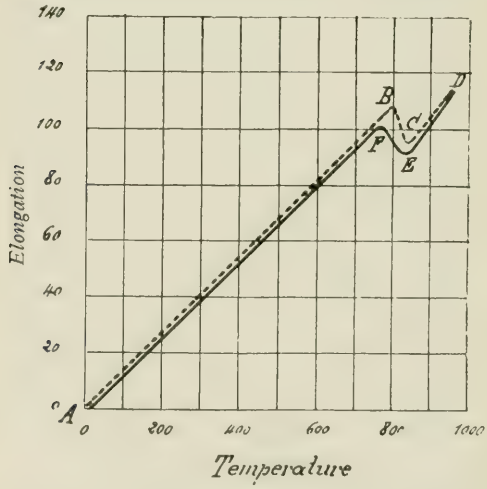


FIG. 324.—Group II. steels, very slow cooling (Grenet).

Group III.—Steels, the transformation temperatures on cooling of which, even at very slow rates of cooling, are distinctly different

[1] Grenet includes in this group the special steels the hysteresis effect of which on slow cooling is less than 150° C.

from the transformation temperatures on heating (curve, Fig. 326). The following steels may be mentioned as industrial examples of Group III. : nickel-chrome steels (3·5—6·0 per cent. Ni+1–2·0 per cent. Cr, and less than 0·65 per cent. C). The chromium may be partially or totally replaced by manganese, tungsten, or molybdenum.

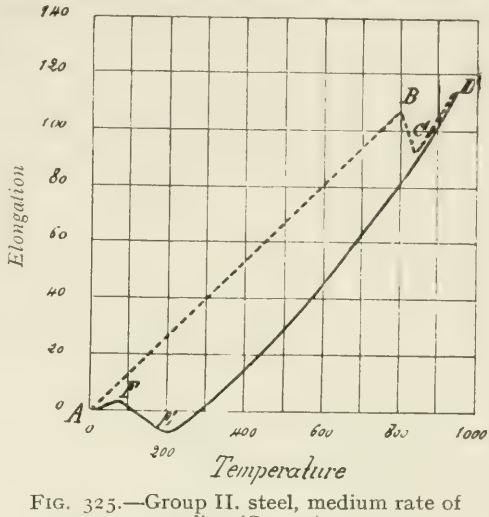


FIG. 325.—Group II. steel, medium rate of cooling (Grenet).

The transformation on cooling may occur at any temperature between the atmospheric temperature and the transformation temperature on heating. This depression of the transformation point is not, however, proportional to the content of the special element added; the addition of 1·7 per cent. Cr to a 4 per cent. Ni steel lowers the transformation point on cooling from 600° to 200°, but further additions of chromium depress the transformation very slowly; thus in the case of those steels in common use, a slight variation in the chemical composition (1 per cent. Ni+1 per cent. Cr) is sufficient to change the transformation on cooling from 700° C. to 300° C.

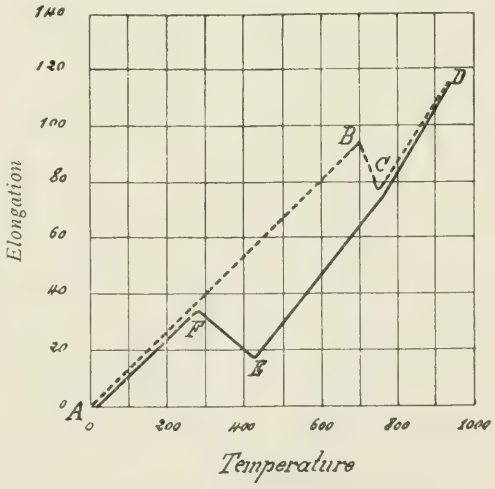


FIG. 326.—Group III. steels (Grenet).

As there is always a depression of the transformation point, no matter how slow the rate of cooling, any heating of the steel above the transformation point on heating, produces a quenching or hardening effect; to soften these steels, they must be subjected to a form of tempering, by heating them *below* the transformation point on heating.

Group IV.—Steels having transformation temperatures on cooling below the atmospheric temperature (curve, Fig. 327). The steels remain on the stable condition at high temperatures.

Examples: Steels of high nickel and manganese content. In certain instances, cooling below the atmospheric temperature brings about the transformation (Fig. 328). These steels are able to undergo reversible magnetic transformations, but such transforma-

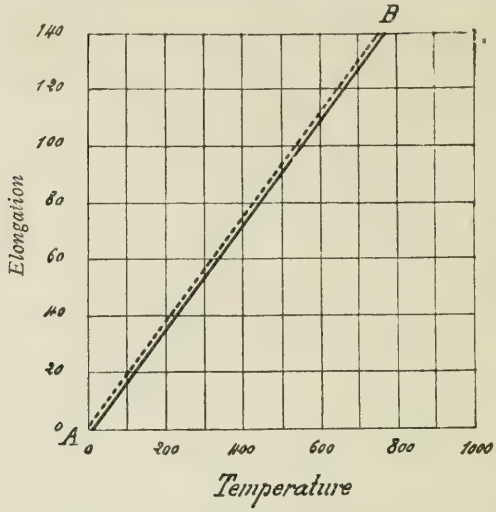


FIG. 327.—Group. IV. steels (Grenet).

tions, as previously stated, are not shown in a marked manner by thermal analysis or in the microscopic structure.

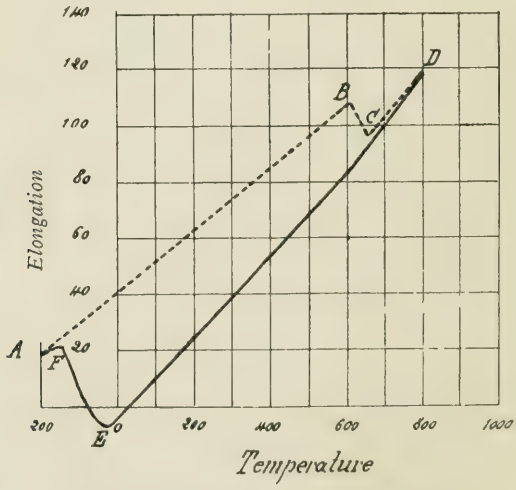


FIG. 328.—Group V. steels (Grenet).

Classification according to Microscopic Structure.—One of the chief points that will be noted in the microscopical examination of special steels is the fact that their structure is described without introducing constituents other than those already described in the

case of ordinary annealed and quenched carbon steels ; an exception is made in the case of the double carbides, which, however, could be included as cementite.

It has only been possible to restrict the terms in use by increasing or broadening the distinctive characteristics of the various constituents ; the definitions previously given will still be applicable, but it must be noted that the constituents of variable concentration (austenite, martensite, troosite, osmondite, carbides . . .) will have chemical properties and consequently etching effects or colorations dependent on their chemical composition, and therefore on their carbon content and the content of any special element they contain ; thus martensite of any definite carbon content is less readily coloured by etching when it contains nickel ; similarly carbide containing tungsten is less readily etched by sodium picrate, as the tungsten content increases.

Therefore the descriptions of the constituents of carbon steels, already given (p. 137) will apply equally to the special steels, and it only remains to give a short description of the double carbides and pure austenite which are met with in special steels, and which have not yet been described.

Pure Austenite.—Appears as crystal grains (polygonal structure), similarly to all solid solutions. If the carbon content of the solid solution is not too low, it is possible, by prolonged etching with ordinary acid reagents, to produce all the spectrum colours on the grains, the colour produced being dependent on the time of etching and orientation of the respective grains ; this effect offers a means of distinguishing austenite from ferrite. A further distinctive characteristic of austenite is the frequent twinning of the crystals. Various other minor characteristics have been suggested by certain authors to distinguish the austenites of nickel, manganese, chromium and even the martensites of these various metals ; these are frequently only individual differences observed in the examination of certain specimens and have no basis for their general application.

Carbides.—Appear separately as small grains, usually rounded but sometimes of geometric outline or as filaments appearing in relief after polishing. They are not attacked by the usual etching reagents, but are attacked and coloured in some instances (similarly to cementite) by sodium picrate. Certain carbide steels remain unaffected by most chemical reagents, and are only attacked by powerful reagents such as molten potassium bisulphate, aqua regia, and even then the carbide constituent remains unaffected.

Diagrams.—The microscopic study of the special steels or alloy steels has been dealt with in a special treatise by one of the authors [1]

[1] Guillet, " Les Aciers spéciaux," 2 vols., Paris, Dunod and Pinat, 1904, 1905.

in the form of diagrams showing the structure of these alloys at ordinary temperature, after ordinary annealing, as a function of the carbon content and the content of the special elements present. These diagrams are not equilibrium diagrams; they outline the areas occupied by the various transitional constituents (martensite, troostite, etc.) and permit of a comparison of the various steels under similar annealing conditions. By their use it is possible to form an estimate of the modifications in structure that may occur in a given series of steels and also the variation in mechanical properties.

The following brief account of the special steels will be limited to the ternary alloys in more general use and will include nickel steels, manganese steels, silicon, chrome, tungsten, molybdenum, and venadium steels. In each, there will be considered: the effect of the special element on the transformation points; the structural diagram; the general variation in properties of the steel.

Nickel Steels

Transformation Points.—Nickel lowers the transformation points and increases the hysteresis effect.

Low Carbon Steels.—1. The addition of nickel to a steel simultaneously lowers the three points A_3, A_2, A_1. With 4 per cent. nickel the A_3 and A_2 points merge into one point; with 8 per cent. nickel present the A_3, A_2, and A_1 points combine (Osmond, carbon content 0·16 per cent. C).

2. The complete investigation of the magnetic transformation of the iron-nickel alloys of low carbon content by numerous investigators has resulted in their subdivision into two classes.

(*a*) Up to 25 per cent. nickel, the hysteresis effect is important and increases greatly with the nickel content. These steels are termed *irreversible;* at the same temperature they may exist in the magnetic or non-magnetic condition according to their previous treatment.

(*b*) Above 25 per cent. nickel, the hysteresis of the magnetic transformation has a maximum of 100° and the transformation curve rises to a maximum and then falls to the magnetic transformation point for nickel. These alloys are termed *reversible.* The diagram, Fig. 329, illustrates these phenomena; the result of Dumas' determinations has been to extend these curves beyond their point of intersection; thus a steel containing 27·72 per cent. Ni which is practically non-magnetic at ordinary temperatures, becomes reversibly magnetic in solid carbon dioxide and irreversibly magnetic in liquid air.

The tremendous transformation hysteresis effect exhibited by the irreversible nickel steels indicates that there is a large interval

between the transformation temperature on cooling and the equilibrium temperature. Thus it is only by exceptionally slow cooling that it is possible to obtain equilibrium structures; by this means are obtained the constituents of meteoric irons: kamacite, taenite and plessite, but they are never obtained in ordinary practice and can only be artificially produced under exceptional conditions (Bénédicks).

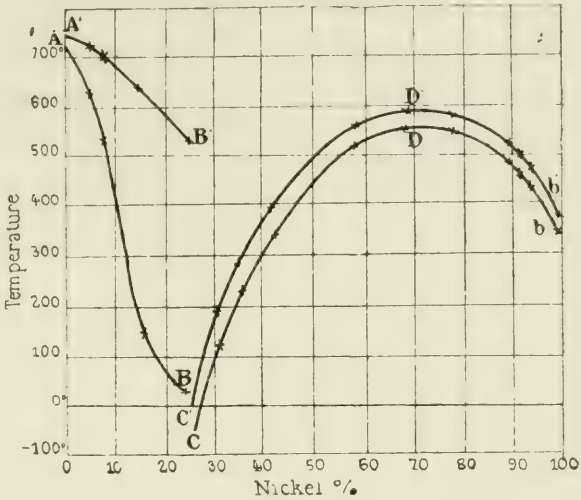


FIG. 329.—Magnetic transformation points of nickel steels (Osmond).

Medium Carbon Steels.—The addition of carbon and manganese considerably depresses the transformation points (Dumas). The thermo-electric determinations of Boudouard have shown that whereas 30 per cent. nickel is necessary to cause the disappearance of the transformation point on cooling when 0·12 per cent. C is present, 9·79 per cent. nickel is sufficient to produce the same effect with 1·05 per cent. C present.[1]

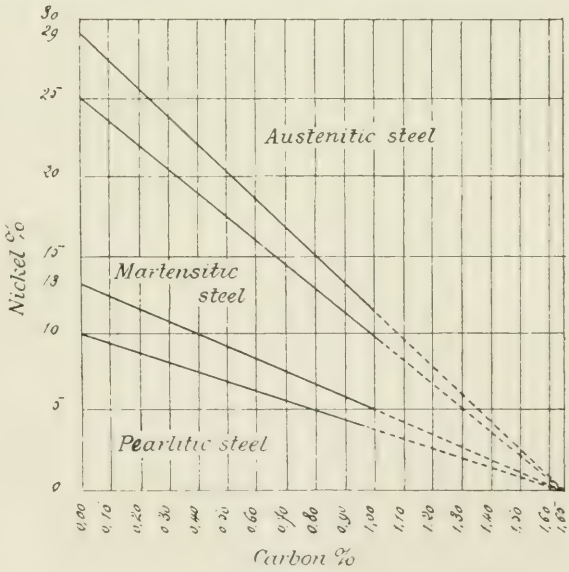


FIG. 330.

Microstructure.—According to their nickel and carbon contents, the nickel steels consist of pearlite (associated with ferrite or cementite according to the carbon content)—termed pearlitic nickel steels—martensite or austenite.

[1] Dejean, by recent determinations, has shown the splitting up of the transformation point on cooling, in the case of nickel steels, in accordance with the general phenomenon mentioned on p. 181 ("Special steel," Group III.), and pp. 194, 196, 197.

The greater the amount of carbon present, the less the amount of nickel required to pass from one structure to the other. These results are due to the effects produced on the transformation points (cooling).

The table and the diagram, Fig. 330, indicate the microstructures of the normal steels after ordinary annealing.

Description.	Carbon content below 0·12 per cent.	Carbon content below 0·80 per cent.
Pearlitic	$Ni < 10$	$Ni < 5$
Martensitic	$10 < Ni < 27$	$5 < Ni < 15$
Austenitic	$Ni > 27$	$Ni > 15$

Figs. 331–334, Pl. LXI.; Figs. 335, 336, Pl. LXII., illustrate typical microstructures (*see* p. 176).

The change from one class to the other occurs progressively; in the diagram are included areas corresponding to the simultaneous existence of pearlite and martensite or martensite and austenite. The different areas are divided by straight lines which if extended in one direction meet approximately at a point. It should be noted that nickel reduces the grain size and gives the pearlite a finer structure.

On quenching, the pearlitic nickel steels become martensitic. The martensitic steels remain martensitic or tend to become austenitic after similar treatment; other conditions being constant, the quenching effect is more pronounced the greater the nickel content. The austenitic steels are not affected by quenching, except those near the martensitic area, which become partially martensitic on quenching.

Figs. 337, 338, Pl. LXII.; Figs. 339, 340, Pl. LXII., illustrate the effects of heat treatment (*see* p. 176).

Cold-work converts the non-magnetic steels into the magnetic variety and brings about the formation or development of cleavage planes and martensitic needles and zigzags within the austenite polyhedra (Figs. 341–342, Pl. LXIV.). It should be noted that the transformation into the acicular structure, which is accompanied by an increase in volume, may be seen in relief on the partially polished specimen before etching (Fig. 345, Pl. LXIV., p. 176).

In all cases of cold-work, internal strain, or rapid cooling, the appearance of martensite needles is accompanied by the return of the magnetic properties.

Connection between the Microstructure and the Properties of the Metal.—It is impossible in the present instance to enter into a full description of the properties of special steels, and in the case of nickel steels a typical example will be chosen to illustrate the

relation between the properties and the microstructure (structural diagram).

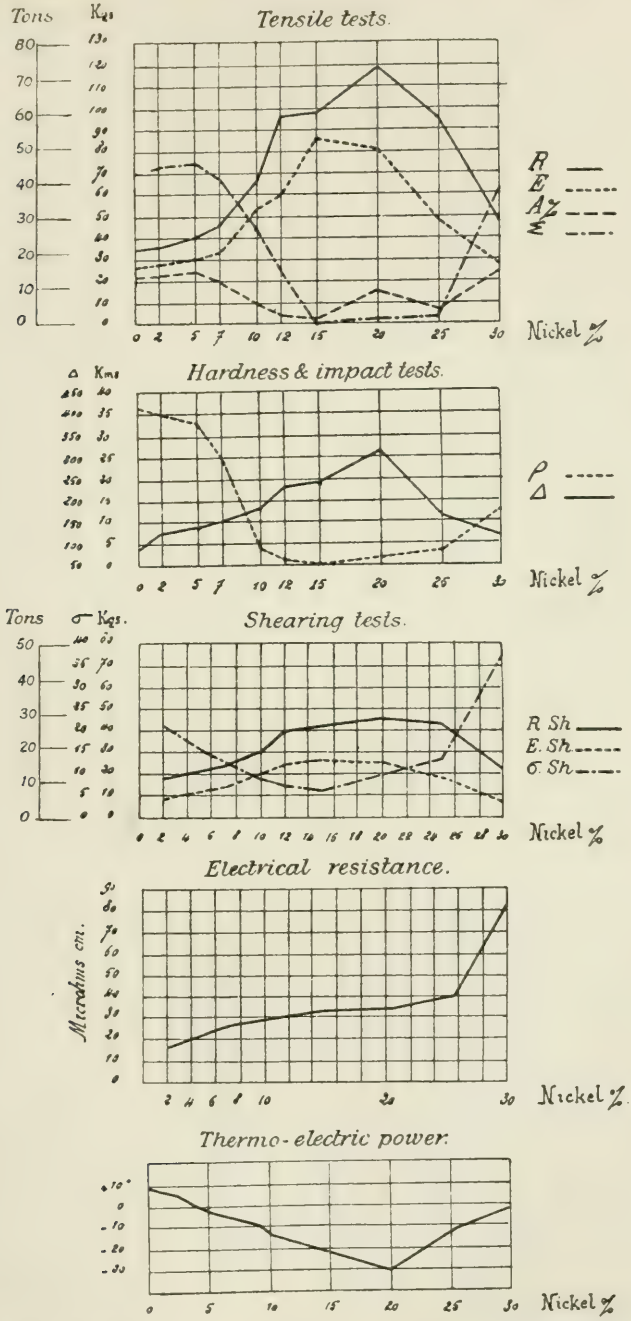


FIG. 347.—0·12 per cent. C steel. Variations in the properties with varying nickel content: tensile tests (Guillet), impact and hardness tests (Guillet), shearing tests (Portevin), electrical resistance (Portevin), thermo-electric power (Dupuy and Portevin). Impact Tests: 1 Km.=7·233 ft.-lbs.

If a series of steels, of increasing nickel content and approximately constant carbon content, are examined, a rapid change in

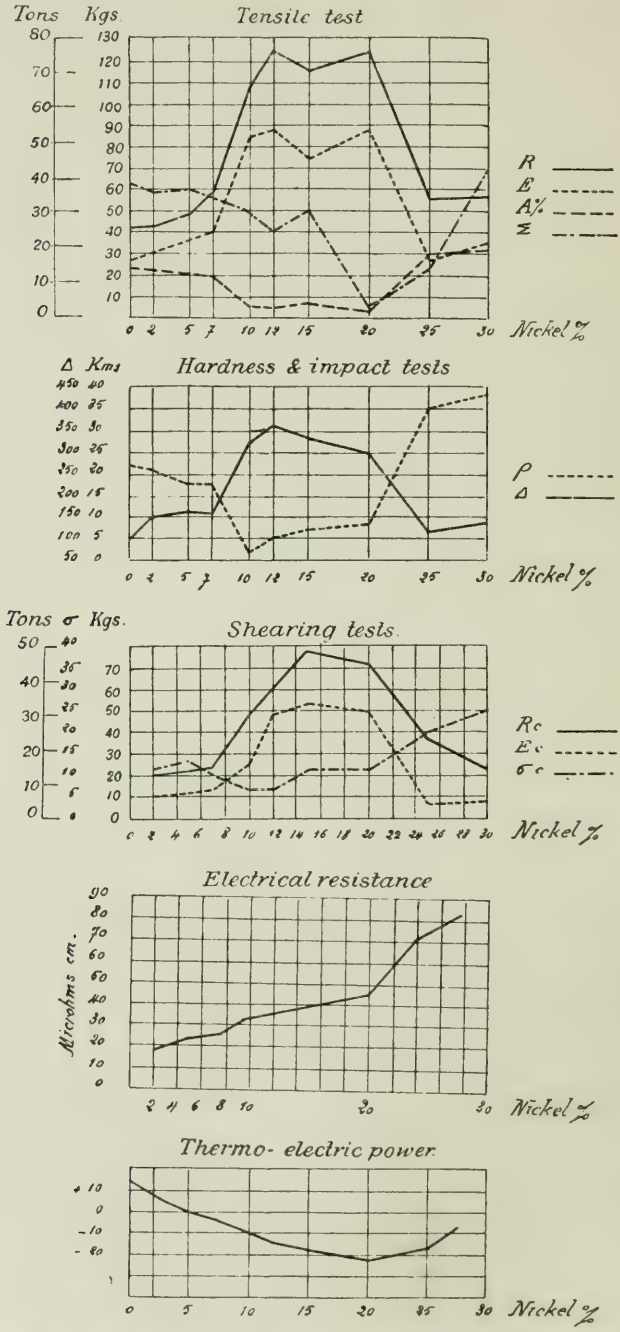
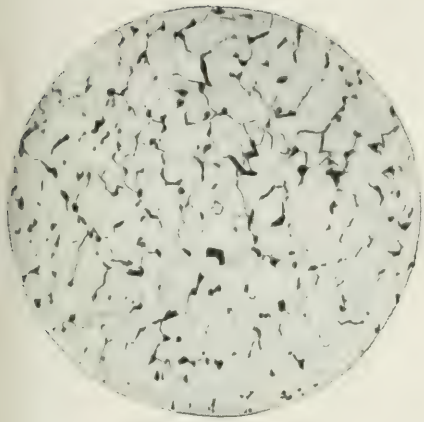
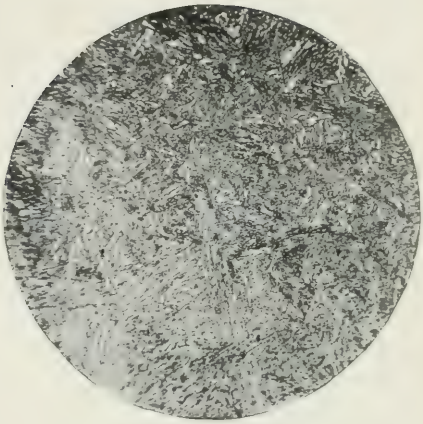


FIG. 348.—0·25 per cent. C steel. Variations in the properties with varying carbon content: tensile tests (Guillet), impact and hardness tests (Guillet), shearing tests (Portevin), electrical resistance (Portevin), thermo-electric power (Dupuy and Portevin). Impact Tests: 1 Km.=7·233 ft.-lbs.

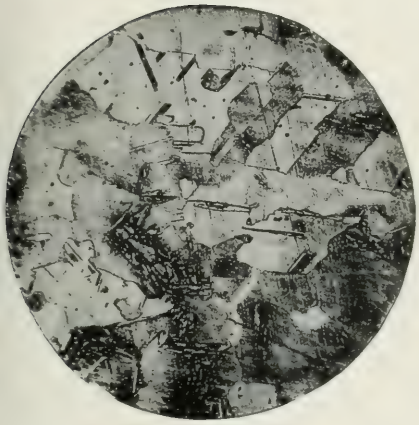
NICKEL STEELS.



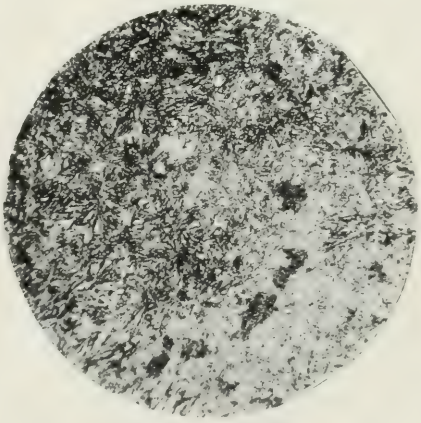
(C = 0·12 ; Ni = 2·0.)
FIG. 331.—Pearlite and ferrite.
Etchant: Picric acid.
(× 300.)



(C = 0·12 ; Ni = 15·0.)
FIG. 332.—Martensite.
Etchant: Picric acid.
(× 300.)

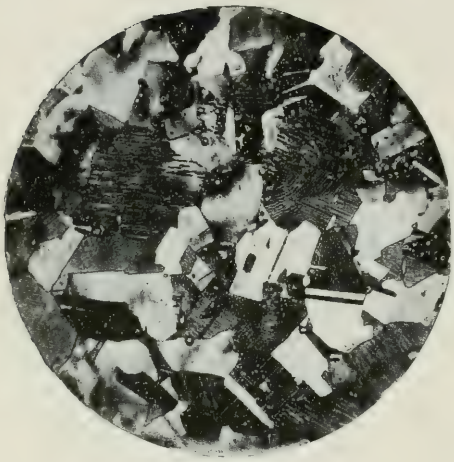


(C = 0·12 ; Ni = 30.)
FIG. 333.—Austenite and a little martensite.
Etchant: Picric acid.
(× 300.)

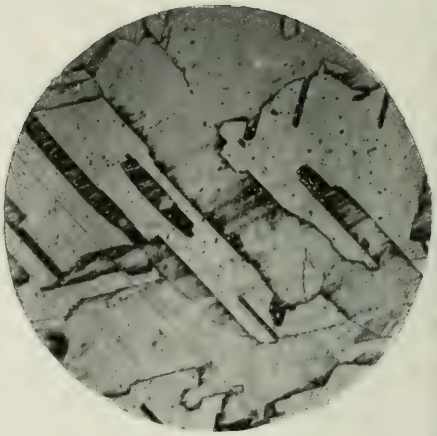


(C = 0·8 ; Ni = 7.)
FIG. 334.—Martensite-austenite.
Etchant: Picric acid.
(× 300.)

NICKEL STEELS (*cont.*).



(C = 0·80; Ni = 25.)
FIG. 335.—Pure austenite showing twinning.
Etchant: Picric acid.
(× 300.)



(C = 0·52; Ni = 92·3.)
FIG. 336.—Pure austenite.
Etchant: Picric acid.
(× 300.)

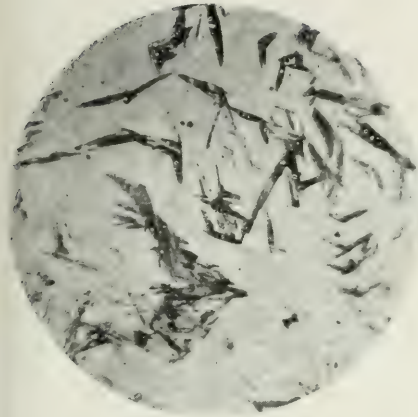
Effect of heat treatment.

(C = 0·12; Ni = 25.)
Quenched from 800° C.
FIG. 337.—Apparent austenite crystals converted to martensite.
Etchant: Picric acid.
(× 300.)

(C = 0·25; Ni = 25.)
Quenched from 800° C.
FIG. 338.—Austenite-martensite.
Etchant: Picric acid.
(× 300.)

NICKEL STEELS (*cont.*).

Effect of heat treatment (*cont.*).



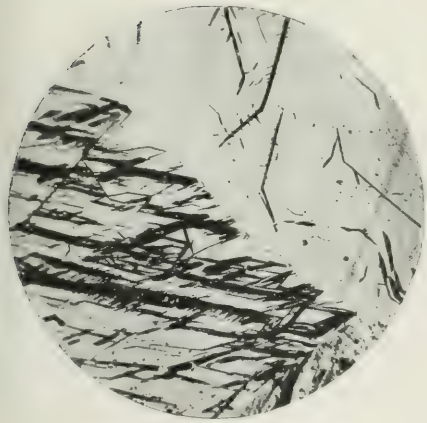
(C = 0·25 ; Ni = 25·0.)
Annealed at 900° C. for 4 hours.

FIG. 339.—Needles of martensite.
Etchant : Picric acid.
(× 300.)

(C = 0·80 ; Ni = 0·20.)
Annealed at 900° C. for 4 hours.

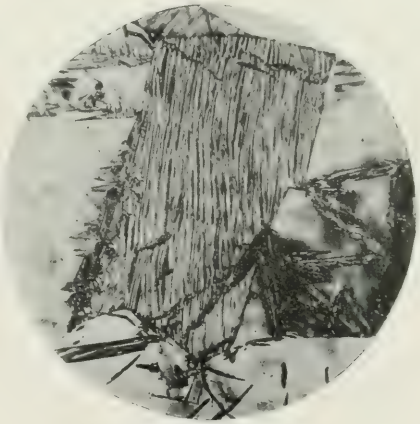
FIG. 340.—Austenite-martensite.
Etchant : Picric acid.
(× 300.)

Effect of cold-work.



(C = 0·80 ; Ni = 12.)
Cold worked.

FIG. 341.—Acicular martensite.

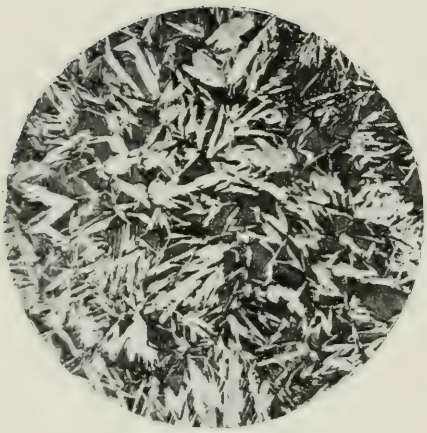


(C = 0·80 ; Ni = 15.)
Cold worked.

FIG. 342.—Crystal of austenite showing striations.
Etchant : Picric acid.
(× 300)

NICKEL STEELS (*cont.*).

Treatment at low temperatures.

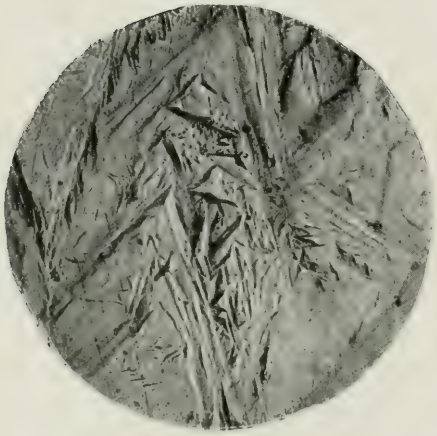


(C = 0·80 ; Ni = 15·0.)
Cooled to −40° C.

FIG. 343.—Austenite martensite.
Etchant: Picric acid.
(× 300.)

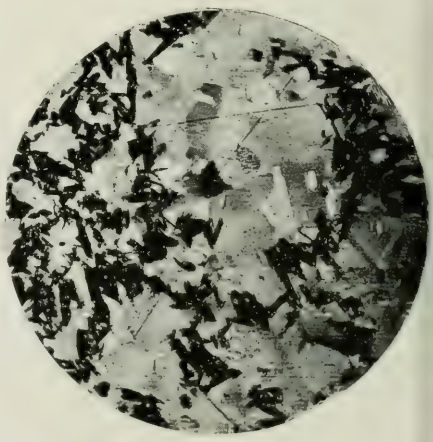
(C = 0·80 ; Ni = 15·0.)
Cooled to −20° C.

FIG. 344.—Austenite-martensite.
Etchant : Picric acid.
(× 300.)



(C = 0·80 ; Ni = 15·0.)
Cooled in liquid air.
Unetched.

FIG. 345.—Martensite shown in relief.



(C = 0·80 ; Ni = 20·0.)
Cooled to −70° C.

FIG. 346.—Austenite and black needles of martensite.
Etchant : Picric acid.
(× 300.)

the properties will be observed on passing from one class to the other (pearlitic—martensitic, etc.). Thus, in the case of steels containing approximately 0·12 per cent. C and 0·25 per cent. C, it is possible, by grouping the results in the form of diagrams (Figs. 347, 348), to observe important changes in the mechanical properties due to the appearance of martensite and austenite ; the variation of the electrical properties, on the contrary, is due to the presence of austenite, which causes the decided change in the slope of the curves.

Analogous variations are similarly revealed, by the examination of series of steels of other carbon contents, but such changes occur at other values of the nickel content in accordance with the changes in the microstructure indicated by the diagram.

As a general rule, the chief characteristics of the martensitic nickel steels are : high ultimate stress, high elastic limit, low percentage elongation, and great hardness. With steels of similar microstructure, for example pure martensitic steels, the properties are dependent on the nickel and carbon contents.

The coefficient of expansion is an important property of nickel steels. The coefficient of expansion of the reversible alloys of low carbon content (0·2 per cent. C) shows considerable variation as the nickel content changes from 28 to 45 per cent. Ni ; the expansion reaches an extremely low minimum value with 36 per cent. Ni, hence the employment of this alloy under the name of Invar in the manufacture of measuring instruments, clocks, and other instruments of precision.

Manganese Steels

Transformation Points.—Manganese depresses the transformation points ; there is, as with nickel, a simultaneous depression and merging together of the several transformation points. With a carbon content of 0·4 per cent. C, and a manganese content above 2 per cent. Mn, only a single transformation, $Ar_{3\cdot2\cdot1}$, will be observed (Osmond) ; further, the hysteresis effect is considerably increased, as in the case of the nickel steels. The following figures may be noted in this connection (Dumas) :—

C	Mn	Transformation points.	
		Heating.	Cooling.
0·35	3·09	672°	425°
0·07	8·29	660°	175°

The transformation point on heating being but little depressed, it will be possible to bring about the transformation by tempering ; thus, by heating for two hours at 550° C., a steel of high carbon

content and containing 13 per cent. Mn is changed from the non-magnetic to the magnetic state (Le Chatelier).

The rapid depression of the transformation point with increasing manganese content leads to the conclusion that with increasing manganese content martensitic steels will first be obtained, and finally austenitic steels when the transformation temperature is below the atmospheric temperature. This is illustrated by the structural diagram constructed by one of the authors [1] (Fig. 349).[2]

Microstructure.—The manganese steels may be divided into three main classes in a similar manner to the nickel steels :—

Description (class).	Under 0·2 per cent. C.	Under 0·8 per cent. C.
Pearlitic	$Mn < 5$	$Mn < 3$
Martensitic or troostitic ..	$5 < Mn < 12$	$3 < Mn < 7$
Austenitic	$12 < Mn$	$7 < Mn$

The diagram (Fig. 349), which illustrates the microstructure of normally annealed steels, is analogous to that given in the case of nickel steels ; two observations may be made in reference to these steels:

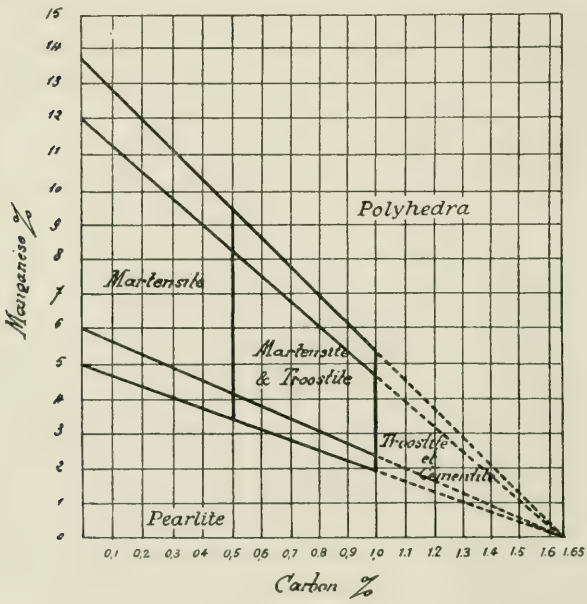


FIG. 349.

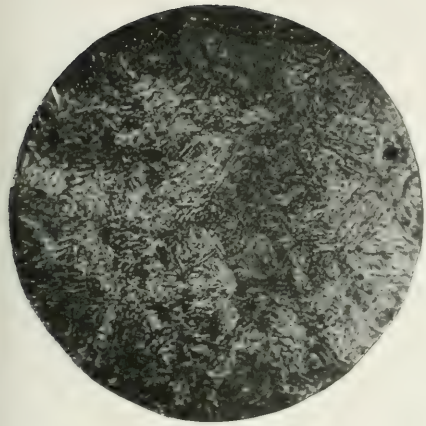
1. The change of class or type, for the same carbon content, occurs at a much lower manganese content than nickel content.

2. The second class or type is either a pure martensitic steel, martensite mixed with troostite or troostite intermixed with cementite ; this class therefore has three sub-divisions dependent on the carbon content.[2]

[1] Guillet, " Les Aciers spéciaux," Dunod and Pinat.

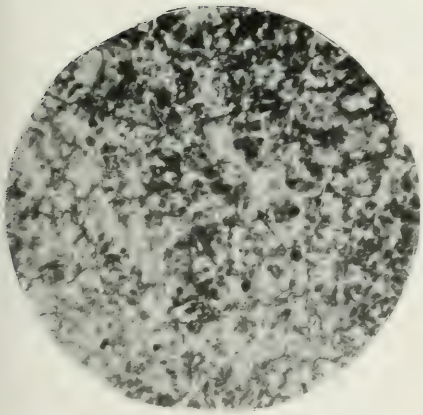
[2] Dejean has recently carried out a complete investigation of the transformation points of manganese steels ; besides confirmation of the generally accepted fact as to the discontinuity in the depression of the transformation point, this research has served to establish a structural diagram which is, in the main outline, similar to that of Fig. 349, but has the addition of a line limiting the area of the existence of troostite (ref. *Revue de Met.*, Sept., 1917. Refer also for the last addition, Portevin, *C. R.*, 165, 62, 1917).

MANGANESE STEELS.

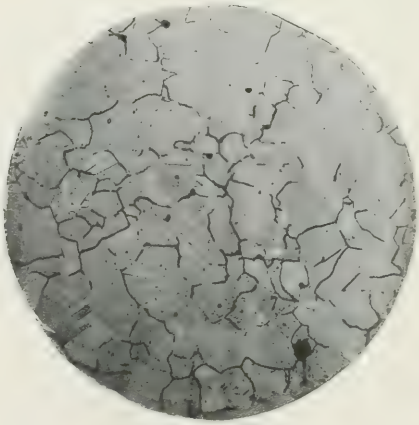


(C = 0·12 ; Mn = 6.)
FIG. 350.—Martensite.
Etchant : Picric acid.
(× 200.)

(C = 0·12 ; Mn = 14·5.)
FIG. 351.—Austenite.
Etchant : Picric acid.
(× 200.)

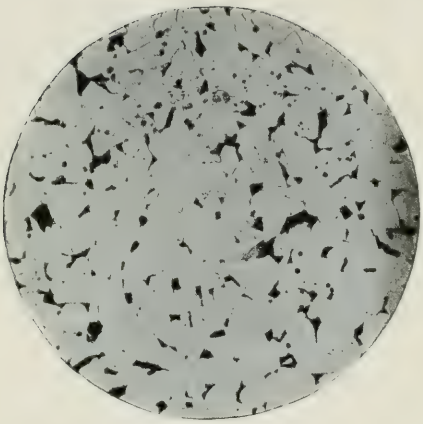


(C = 0·60 ; Mn = 5·0.)
FIG. 352.—Troostite, dark.
Etchant : Picric acid.
(× 200.)

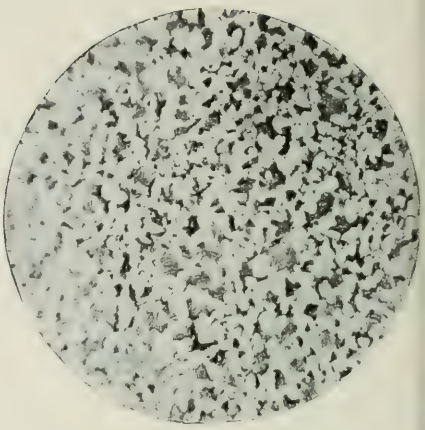


(C = 0·80 ; Mn = 10.)
FIG. 353.—Austenite.
Etchant : Picric acid.
(× 200.)

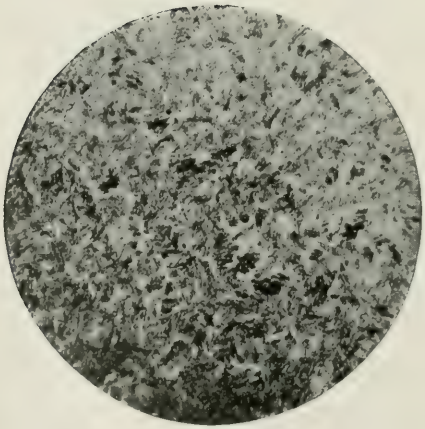
CHROME STEELS.



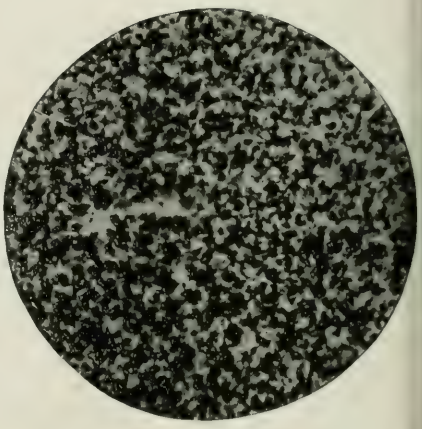
(C = 0·20; Cr = 0·7.)
FIG. 355.—Pearlite and ferrite.
Etchant: Picric acid.
(× 200.)



(C = 0·20; Cr = 4·5.)
FIG. 356.—Pearlite and ferrite.
Etchant: Picric acid.
(× 200.)



(C = 0·20; Cr = 9·0.)
FIG. 357.—Nearly pure martensite.
Etchant: Picric acid.
(× 200.)



(C = 0·80; Cr = 7·3.)
FIG. 358.—Troostite dark.
Etchant: Picric acid.
(× 200.)

As a general rule, the microscopic study of manganese steels is more difficult than the study of nickel steels. The presence of manganese affects the action of the various etching reagents, which tend to produce rapid and unequal coloration and oxidation effects; moreover, the structures obtained are not as clearly defined as the nickel steel structures. Figs. 350–353, Pl. LXV., illustrate the characteristic structures of manganese steel. The effects of heat treatment, quenching and annealing, and cold work are comparable with the effects produced in the case of nickel steels; it may be noted that the troostitic steels give on quenching either pure martensite or martensite mixed with a little austenite.

Relation between the Microstructure and the Mechanical Properties.—The mechanical properties of the manganese steels are analogous to those of the nickel steels and are, as in the latter case, directly related to the microstructure.

It may be mentioned that the pearlitic manganese steels are not more brittle than ordinary steels, at least when of low carbon content; whereas the austenitic manganese steels are extremely difficult to work owing to their peculiar toughness.

Chrome Steels

Transformation Points.—According to Osmond, the magnetic transformation point remains practically constant; inversely, the transformation point (cooling) is clearly affected by the temperature to which the steel is heated.

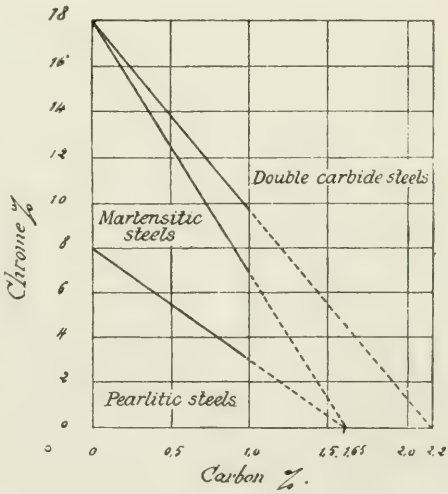


FIG. 354.

The examination of these steels containing up to 9·63 per cent. Cr has enabled Nesselstrauss to obtain the following results (with a mean cooling rate of 3·65° C. per minute):—

1. Chromium depresses the Ar_3 point and finally causes its disappearance; the disappearance occurs at lower chromium contents, the higher the carbon content in hypo-eutectoid steels (5 per cent. Cr with 0·2 per cent. C present).

2. Chromium raises the Ar_1 point, the thermal effect being at a maximum with 5 per cent. Cr present.

3. Chromium decreases the speed of the transformations.

Microstructure.—Chrome steels are to a certain extent an intermediate type between the nickel or manganese steels and the tungsten or molybdenum steels. The chrome steels include pearlitic and martensitic steels as in the case of nickel and manganese steels, and also double carbide steels corresponding to the tungsten and molybdenum steels. The following table gives the microstructures of normal chrome steels according to their chemical composition (Fig. 354).

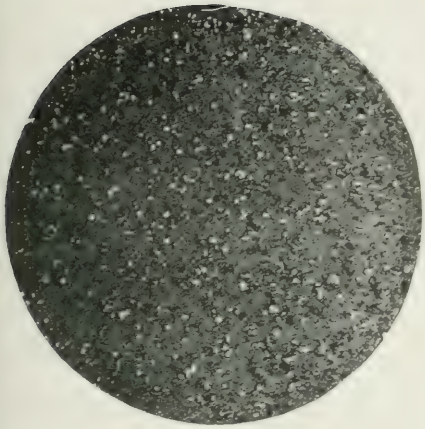
Description (class).	Carbon content under 0·2 per cent.	Carbon content under 0·8 per cent.
Pearlite	$0 < Cr < 7$	$0 < Cr < 3$
Martensite, troostite	$7 < Cr < 15$	$3 < Cr < 10$
Martensite and special constituent ..	$15 < Cr < 20$	$10 < Cr < 18$
Special constituent	$20 < Cr$	$18 < Cr$

Figs. 355–358, Pl. LXVI.; Figs. 359–362, Pl. LXVII.; Figs. 363–364, Pl. LXVIII., show typical microstructures of chrome steels.

The special constituent mentioned in the table is not attacked even by the most active reagents and appears in the form of bright spots or grains (Fig. 359, Pl. LXVII.) which increase in number as the chromium content increases. It may be produced by the cementation of pearlitic and martensitic chrome steels and is etched and coloured by sodium picrate in the case of steels of low chromium content. It consists of a double carbide of iron and chromium. Martensite of definite carbon content etches with greater difficulty the higher the chromium content. Steels with 0·2 per cent. C and over 14·5 per cent. Cr, on etching with picric acid show, besides the bright areas of carbide, polyhedra in the interior of which extremely fine martensitic structure may be developed by further etching with hydrochloric acid, aqua regia diluted with gylcerine or potassium bisulphate. A similar result is obtained with steels containing 0·8 per cent. C and above 9·0 per cent. chromium. The appearance of martensite on increasing the chromium content at first appears contradictory to what has been stated in regard to the transformation points which are raised by increasing chromium contents. But it must not be overlooked that chromium considerably increases the hysteresis effect in such a manner that, at normal rates of cooling, it is possible to obtain martensitic steels if the chromium content is sufficiently high; but under these conditions it should be possible, by slowing the rate of cooling, to raise the transformation range sufficiently to cause the disappearance of the martensitic structure. Experiment has verified this assumption and thus makes it possible to convert the martensitic chrome steels into the pearlitic condition, as illustrated by Fig. 365, Pl. LXVIII.; Fig. 367, Pl. LXIX.; there

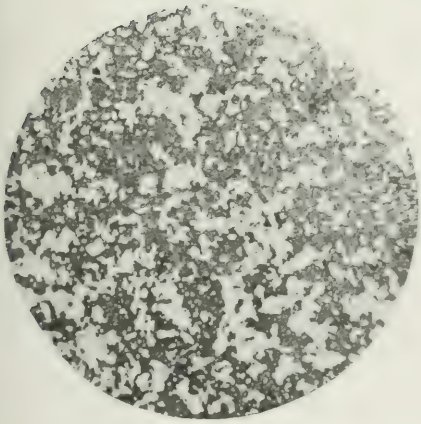
CHROME STEELS (*cont.*).

Carbide steels.

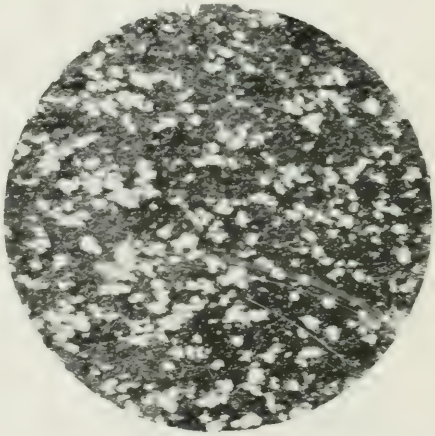


(C = 0·46 ; Cr = 31·7.)
FIG. 359.—White carbide.
Etchant : Picric acid.
(× 200.)

(C = 0·90 ; Cr = 18·6.)
FIG. 360.—Annealed at 1200° C. for 8 hours.
Carbide distributed as a network round the grains.
Etchant : Aqua regia.
(× 200.)



(C = 1·30 ; Cr = 40·2.)
FIG. 361.—White carbide.
Etchant : Picric acid.
(× 200.)



(C = 1·30 ; Cr = 40·2.)
FIG. 362.—The same steel quenched from 1100° C. in air.
Diminution of carbide.
Etchant : Picric acid.
(× 200.)

CHROME STEELS (*cont.*).

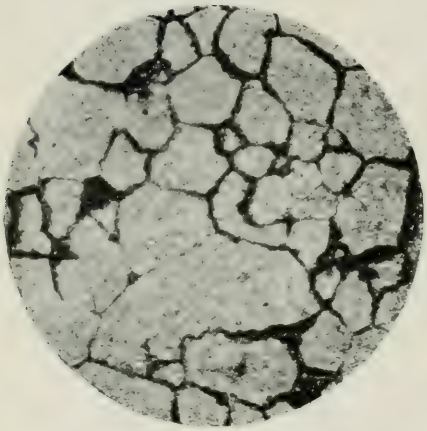


FIG. 363.—Cemented chrome steel, 14·5 % Cr. Dark network of troostite in a background of martensite.
Etchant: Aqua regia.
(× 200.)

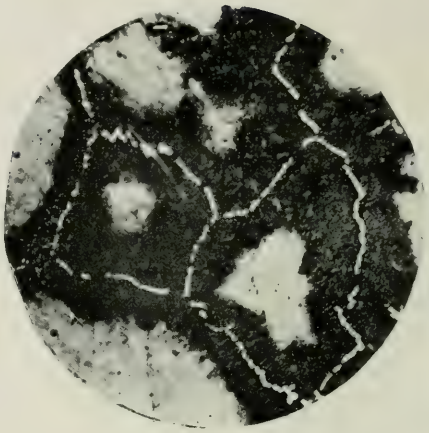


FIG. 364.—Cemented chrome steel, 14·5 % Cr. Carbide, white; troostite, dark.
Etchant: Aqua regia.
(× 200.)

Effect of annealing followed by very slow cooling on martensitic steels.

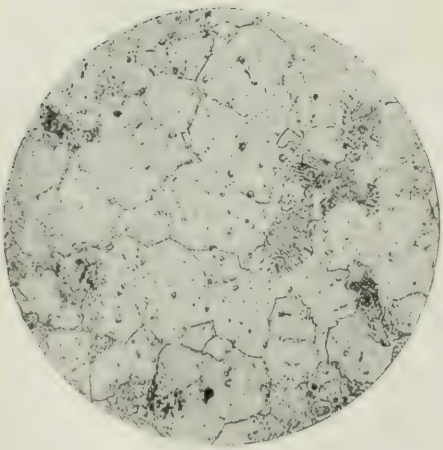


FIG. 365.—Very slowly cooled.

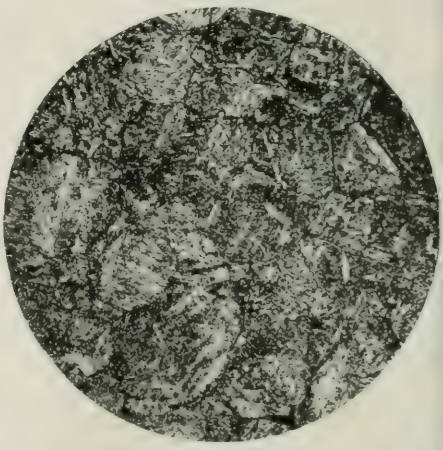


FIG. 366.—Annealed at 1000° C. and cooled in 4 ho

Chrome steel, 0·12 % C.; 17·0 % Cr.
Etchant: Aqua regia + glycerine.
(× 200.)

CHROME STEELS (*cont.*).

Effect on martensitic steels of annealing followed by very slow cooling (*cont.*).

Chrome steel, 0·12 % C; 17·0 % Cr.
Etchant: Aqua regia + glycerine.
(× 1350.)

Fig. 367.—Very slowly cooled.

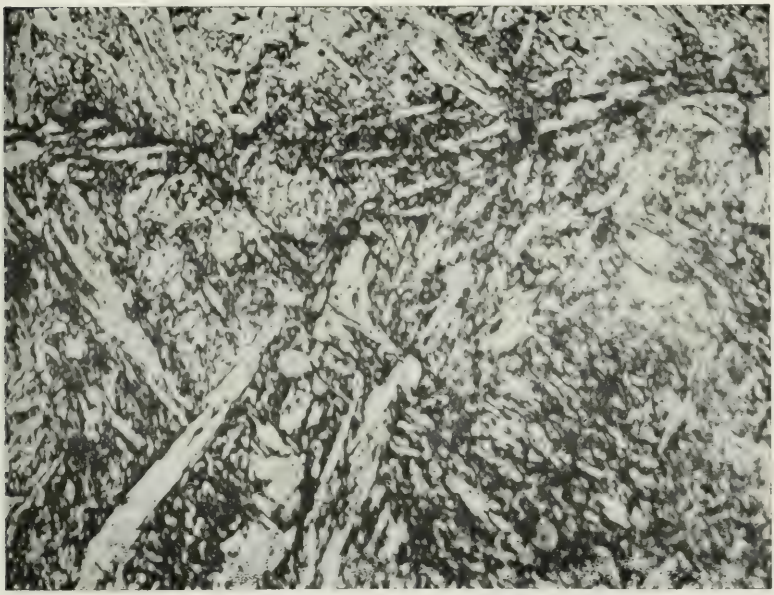
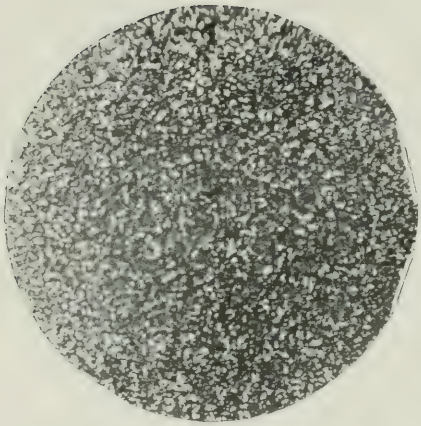


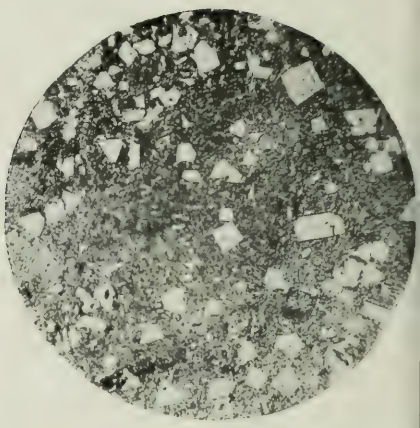
Fig. 368.—Annealed at 1000° C. and cooled in 4 hours.

SPECIAL STEELS.

Tungsten steels.

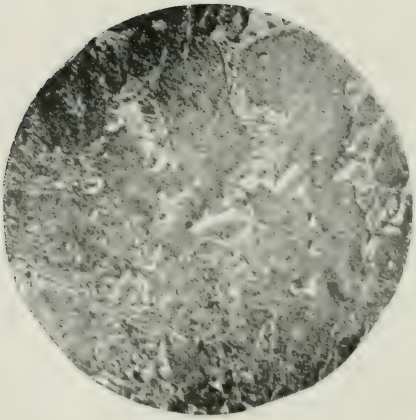


(C = 0·27 ; W = 27·75.)
FIG. 370.—White carbide.
Etchant : Picric acid.
(× 200.)

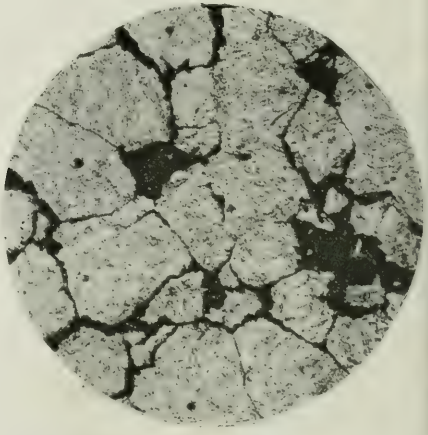


(C = 0·87 ; W = 39·96.)
FIG. 371.—White crystals of carbide.
Etchant : Picric acid.
(× 200.)

Molybdenum steels.



(C = 0·69 ; Mo = 14·64.)
FIG. 373.—White carbide.
Etchant : Picric acid.
(× 450.)



(C = 0·29 ; Mo = 4·50.)
FIG. 374.—Quenched in air from 1200° C.
Troostite, dark.
Etchant : Picric acid.
(× 200.)

is a simultaneous reduction of hardness which, for a steel containing 0·12 per cent. C and 13 per cent. Cr, is reduced to half its original value. Ordinary industrial annealing of a steel in this softened condition restores the martensitic structure (Fig. 366, Pl. LXVIII., and Fig. 368, Pl. LXIX.) and the equivalent hardness; this treatment, therefore, has an effect similar to an ordinary quenching even though the cooling operation may occupy several hours.

Relation between the Microstructure and the Mechanical Properties.—The pearlitic steels possess properties analogous to those of ordinary pearlitic steels; the ultimate strength increases with the chromium content; they are considerably less resistant to impact than ordinary steels; their hardness increases rapidly as the chromium content is raised.

The martensitic steels give very high ultimate stress and elastic limit, and low elongation; they are brittle and easily fractured, but this brittleness is not found in any marked degree in the low carbon steels; they are exceptionally hard and the hardness is due more to the chromium than the carbon content.

Under otherwise constant conditions (Cr content, etc.) the troostitic chrome steels give much lower ultimate strength than the martensitic steels.

The double carbide steels possess a mean ultimate strength and a low elastic limit; they may be compared with austenitic steels, but they give a large percentage reduction of area and a medium elongation; they are soft and very brittle. It will be noted that, with these steels, there is no connection between the brittleness and elongation.

Tungsten Steels

Critical Points.—The positions of the critical points, on cooling, of tungsten steels are largely dependent on the conditions of heating and cooling.

Three examples are given—

1. *Tungsten steel* 0·42 per cent. C + 6·25 per cent. W (Osmond).

After heating to 920° C., two critical points are found at 690° C. and 650° C.

After heating to 1015° C., the first point remains at practically the same temperature (670°), the second is depressed to 625° C.

After heating to 1210° C., the first point is practically indistinguishable, the second remains, greatly accentuated and depressed to 500° C. This lower critical point appears to correspond with the Ar_1 point of carbon steels.

2. *Tungsten steel* 0·85 per cent. C+7·78 per cent. W (Böhler). This steel shows two critical points (710° and 550°); the upper point is only visible when the metal is not heated above 1100° C.;

the lower point only appears when the heating temperature exceeds 1000° C. Between these two temperatures (heating), two critical points are observed on cooling. Therefore the gradual increase of the heating temperature brings about an alteration of the critical points on cooling, the lower critical point only occurring when the temperature during heating has exceeded 1000° C.

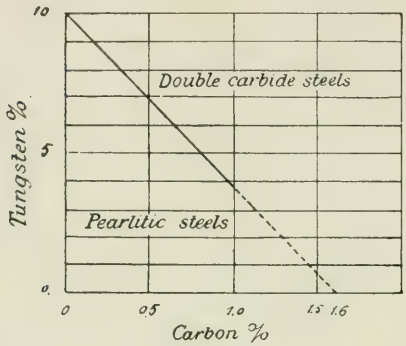


FIG. 369.

3. *Tungsten steel* 3 per cent. W + varying carbon content (Swinden). The critical point Ar_1 is depressed as the temperature during heating is increased, until a practically constant lower limit is reached at about 570° C. for any carbon content. The temperature to which it is necessary to heat the metal to bring this depression to its maximum limit, is higher as the carbon content increases. The rate of cooling appears to be of far less importance than the temperature to which the metal is heated.

Microstructure.—The tungsten steels may be classified as pearlitic and double carbide steels; the steels are classified under those headings in the following table, and in the diagram, Fig. 369.

Description (class).	Carbon content under 0·2 per cent. C.	Carbon content under 0·8 per cent.
Pearlitic	W < 10	W < 5
Double carbide	W > 10	W > 5

Thus, the formation of the double carbide (Figs. 370, 371, Pl. LXX.) occurs at a constant carbon content with increasing tungsten content, and also at a constant tungsten content by increasing the carbon content. It may therefore be produced by the cementation of a pearlitic tungsten steel. The carbide occurs as small rounded globules or fine filaments. It is only attacked by sodium picrate when the tungsten content is comparatively low in value. Quenching tends to cause its disappearance, this effect being proportional to the quenching temperature.

Molybdenum Steels.

Transformation Points or Critical Points.—The results obtained by Swinden may be summarised as follows: So long as the initial temperature on cooling does not exceed a certain definite temperature

termed "depression temperature," T*a*, the normal critical points (cooling) will be found and their position is independent of the temperature or the time of heating. According to the amount this depressed temperature T*a* is exceeded the point Ar_1 is depressed, splits up, and finally assumes a definite lower position when the heating temperature reaches a definite value, which may be termed T*m*. This lower position, which is constant for any given steel, is a function of the molybdenum content, and is unaffected by slow cooling or by stopping the cooling at 800° C.

The temperatures T*a* and T*m* rise slightly as the proportion of carbon increases. In the case of a steel in which the normal critical point has been depressed, it is possible to restore the steel to the normal condition by repeated heating just below the depression temperature. The same result is not so readily brought about by slow heating and annealing. On heating, the normal Ac_1 point is found and no new point has been found corresponding to the "depression" temperature.

Microstructure.—The microstructure of the normal molybdenum steels is analogous to that of the tungsten steels: they consist of pearlitic and double carbide steels (cementitic steels) (Fig. 373, Pl. LXX., p. 181). The classification is shown in the following table and by the diagram, Fig. 372.

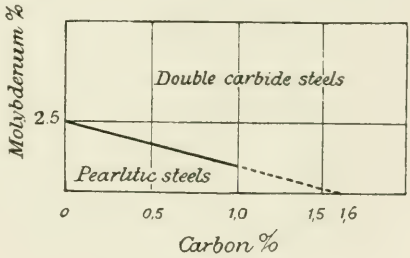


FIG. 372.

The pearlite in these steels has an extremely fine structure; the carbide has a vermiculated appearance (intertwined filaments) and, according to Swinden, has the composition Fe_3C. According to the same author, the pearlite saturation point, above which free

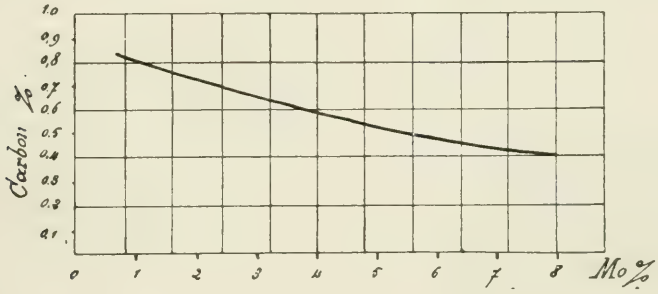


FIG. 375.

carbide appears, is lowered as the molybdenum content increases, as shown by Fig. 375.

Relation between the Microstructure and the Mechanical Properties.—Molybdenum produces similar effects to tungsten on the mechanical properties of a steel, but it requires the addition of four times as much tungsten to produce a given effect.

Vanadium Steels

Transformation Points or Critical Points.—According to Pütz, in steels containing less than 1 per cent. vanadium.

1. A small percentage of vanadium, 0·2 per cent. V, is sufficient to raise the Ar_1 point 10° C., further additions of vanadium producing no additional increase.

2. The point $Ar_{3.2}$ is raised in a similar manner, but in this case the increase is proportional to the vanadium content.

According to results obtained by one of the authors,[1] with steels containing up to 7 per cent. and 10 per cent. V, the following occurs :—

1. With steels containing 0·2 per cent. C, the Ar_3 is at first raised proportionally to the vanadium content and then disappears between 4 per cent. and 7 per cent. V ; Ar_2 is raised in a similar manner but less rapidly.

2. With steels containing 0·8 per cent. C, the Ar_1 remains approximately constant up to 1 per cent. V, above this value it slowly decreases as the vanadium content increases.

According to Arnold and Read, in steels containing 10 per cent. V, the Ar_1 point lies between 1200° and 1400° C.

Microstructure.—The vanadium in steels containing little of this element remains in solid solution in the ferrite, which is more readily attacked (coloured) the greater the amount of vanadium present ; but above a certain definite content, the solid solution being saturated, the vanadium replaces the iron in the carbide and appears in the pearlite as small white particles which are visible after polishing in bas-relief (Figs. 377, 378, Pl. LXXI.). These grains increase in number as the vanadium content increases, and at the same time the pearlite areas decrease and finally disappear.

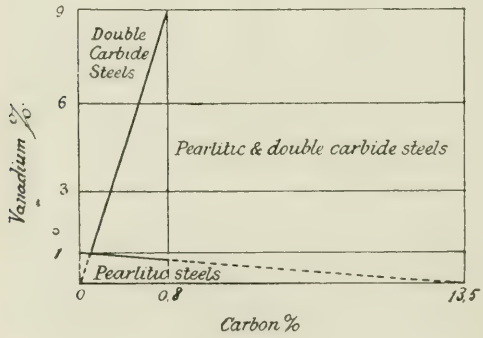


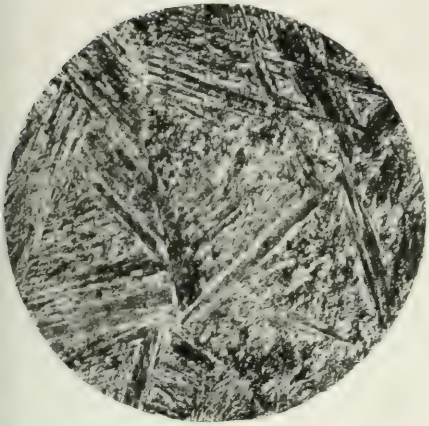
FIG. 380.

The three classes of vanadium steels therefore consist of : pearlite, pearlite and carbide, or carbide, and it should be observed that it is

[1] Portevin, *Revue de Met.*, vol. vi. p. 1352, 1909.

SPECIAL STEELS (*cont.*).

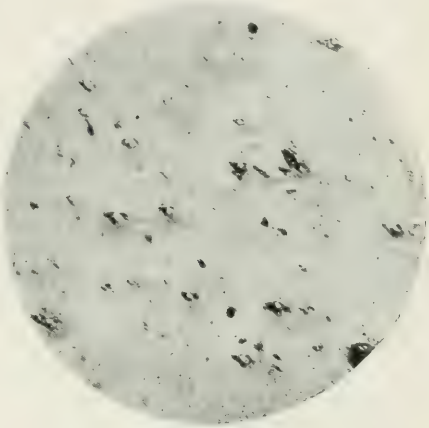
Molybdenum steels (*cont.*).



(C = 0·73; Mo = 0·50.)

FIG. 376.—Quenched in air from 1200° C.
Coarse martensite.
Etchant: Picric acid.
(× 200.)

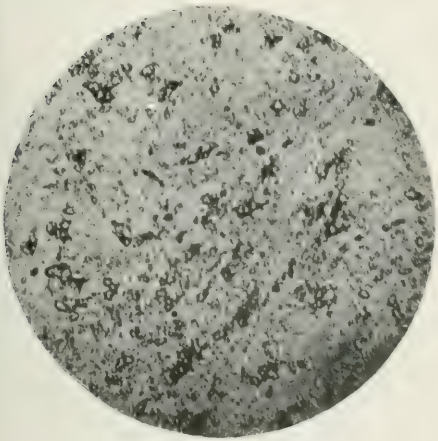
Vanadium steels.



(C = 0·12; Va = 10·27.)

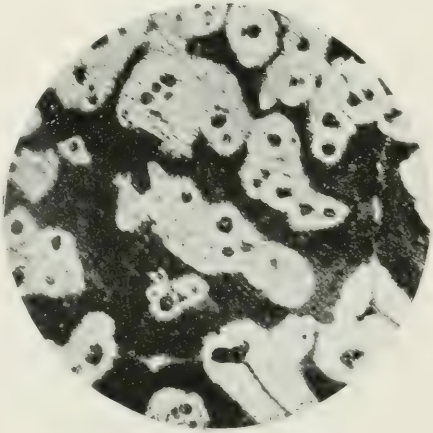
FIG. 377.—Annealed at 1200° C. for 4 hours.
Small grains of carbide.
Etchant: Picric acid.
(× 200.)

Vanadium steels.



(C = 0·74; Va = 7·85.)

FIG. 378.—Carbide appearing as small rounded grains.
Etchant: Picric acid.
(× 200.)

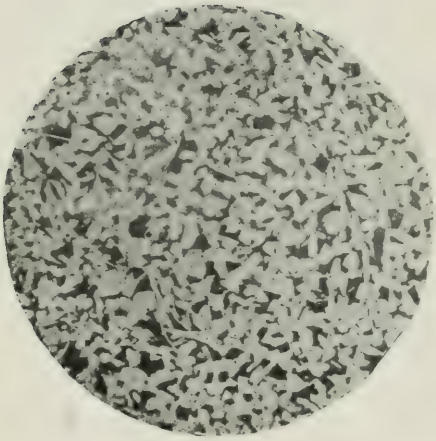


(C = 0·95; Va = 2·89.)

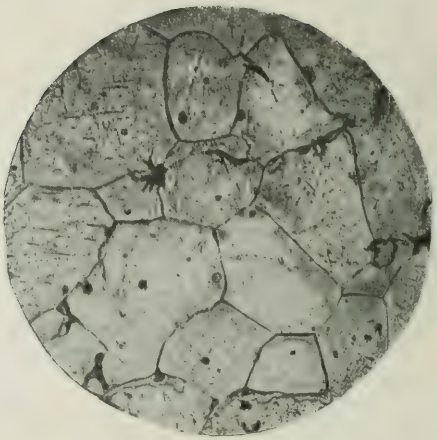
FIG. 379.—Annealed at 1200° C. for 4 hours.
Black specks of graphite in the white ferrite.
Etchant: Picric acid.
(× 200.)

SPECIAL STEELS (*cont.*).

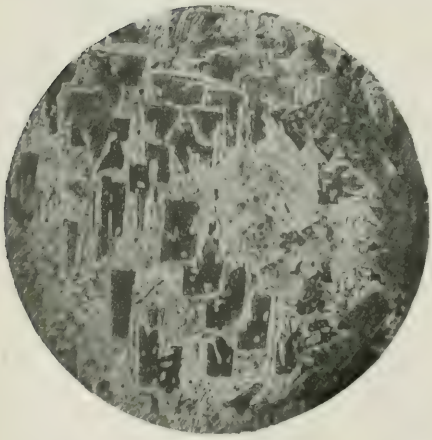
Silicon steels.



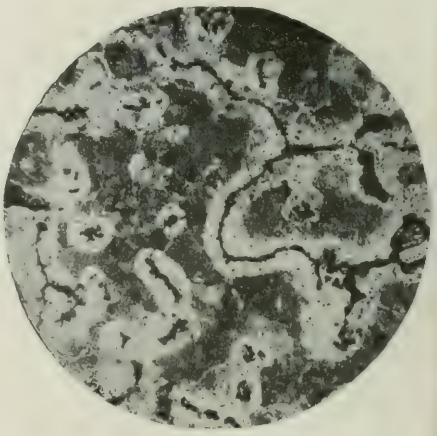
(C = 0·21 ; Si = 0·41.)
FIG. 381.—Ferrite and pearlite.
Etchant: Picric acid.
(× 200.)



(C = 0·22 ; Si = 7·17.)
FIG. 382.—Ferrite and a little graphite.
Etchant: Hydrochloric acid.
(× 200.)



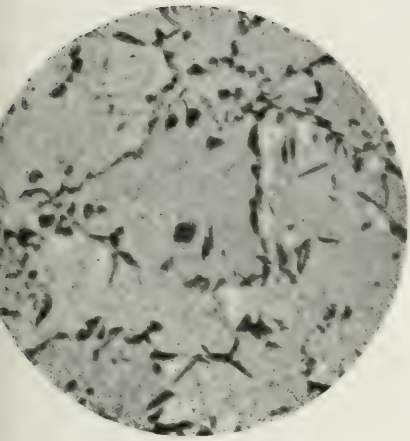
(C = 0·28 ; Si = 5·25.)
FIG. 383.—Crystals of FeSi.
Etchant: Hydrochloric acid.
(× 200.)



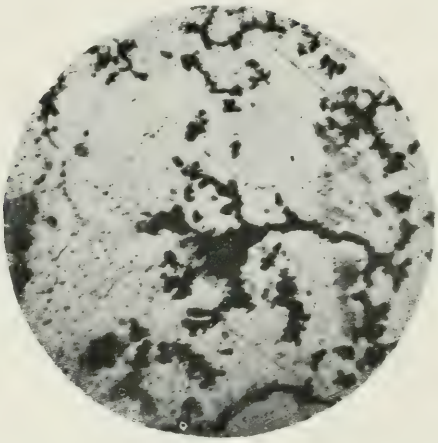
(C = 0·94 ; Si = 5·54.)
FIG. 384.—Graphite, ferrite, pearlite.
Etchant: Picric acid.
(× 200.)

SPECIAL STEELS (*cont.*).

Silicon steels (*cont.*).



(C = 0·28 ; Si = 5·12.)
FIG. 385.—Annealed 2 hours at 900° C.
Graphite, black.
Etchant: Picric acid.
(× 200.)



(C = 0·94 ; Si = 5·54.)
FIG. 386.—Annealed 6 hours at 900° C.
Graphite, black.
Etchant ; Picric acid.
(× 200.)

High speed tool steels.

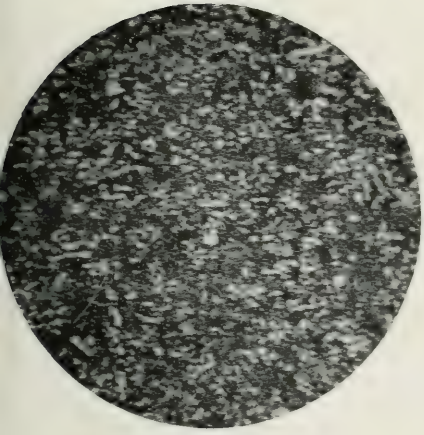


FIG. 387.—High speed steel.
Etchant: Picric acid.
(× 200.)

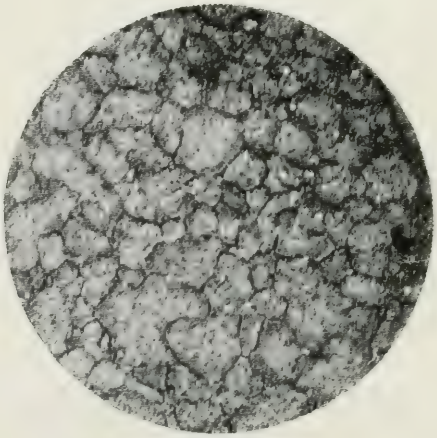


FIG. 388.—Same as Fig. 377.
Quenched in air from 1200° C.
Etchant: Picric acid.
(× 200.)

SPECIAL STEELS (*cont.*).

High speed tool steels (*cont.*).

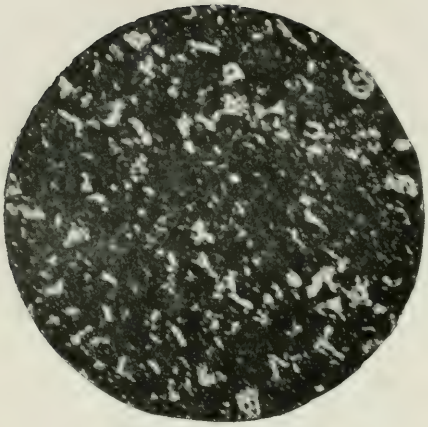


FIG. 389.—High speed steel.
Etchant: Picric acid.
(× 200.)

FIG. 390.—The same as Fig. 389.
Quenched in air from 1200° C.
Etchant: Picric acid.
(× 200.)

Ferro-Alloys.

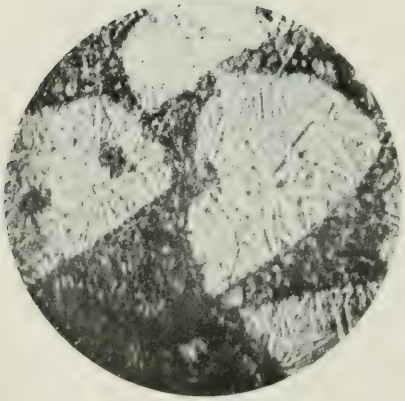


FIG. 391.—Ferro-silicon, 27 % Si.
Needles of FeSi.
Etchant: Hydrochloric acid.
(× 200.)

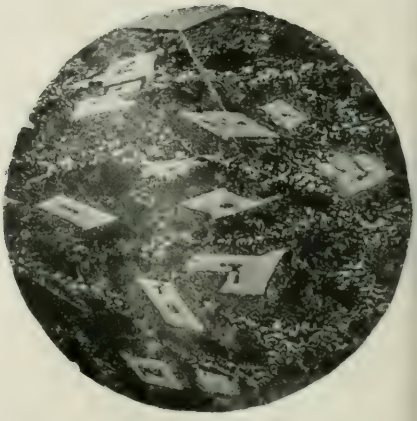


FIG. 392.—Iron-phosphorus alloy: Fe = 88 %
Crystals of Fe_3P surrounded by eutectic.
Etchant: Dilute nitric acid.
(× 200.)

not possible to estimate the carbon content of the pearlitic steels by microscopical examination. Thus the carbide and pearlite steels containing 0·9–1·0 per cent. C very closely resemble those containing 0·6–0·7 per cent. C. According to Arnold and Read, when the vanadium content reaches 6·0 per cent. the carbide only contains vanadium. One of the authors has formed a similar conclusion from the study of the electrical resistance of these alloys.

The table and the diagram (Fig. 380) illustrate the microstructures of the vanadium steels.

Description (class).	Carbon content under 0·2 per cent. C.	Carbon content under 0·8 per cent. C.
Pearlite	$Va < 0·7$	$Va < 0·5$
Pearlite and carbide ..	$0·7 < Va < 3$	$0·5 < Va < 7$
Carbide	$3 < Va$	$7 < Va$

The diagram shows that the greater the carbon content, the greater the vanadium content required to cause all the carbon to exist as carbide. The vanadium carbide rises in the ingots during casting, owing to its low specific gravity; thus segregation is always present in the carbide steels.

Graphite (temper carbon) is produced by annealing (Fig. 379, Pl. LXXI.).

Relation between the Microstructure and the Mechanical Properties.—The pearlitic steels have proportionately higher ultimate strength the greater the vanadium content. The ultimate strengths of steels containing pearlite and carbide decrease as the vanadium contents increases; the brittleness of these steels increases in a similar manner. The carbide steels have comparatively low ultimate strength, low elastic limit, and are very brittle.

Silicon Steels

Transformation Points or Critical Points.—According to Osmond, silicon raises the A_3 point and causes its disappearance when 2 per cent. Si is present; the A_2 point is depressed whilst the A_1 tends to rise and coincide with the A_2 point. The determinations of Charpy and Cornu have confirmed these results and have shown that:—

1. The A_3 point becomes fainter, whilst slowly rising, as the proportion of silicon increases, and finally disappears when the silicon content is approximately 1·5 per cent. Si.

2. The A_2 point is steadily depressed as the silicon content increases but remains practically constant in intensity. In the low carbon alloys the depression is approximately 10–12° C. for 1 per cent. Si.

3. The A_1 point is raised slightly as the silicon content increases, and at the same time it becomes fainter owing to the transformation of the carbon into graphite due to the presence of silicon, and finally disappears when the silicon content exceeds 5 per cent. Si (approx.). Its intensity varies not only with the amounts of carbon and silicon present, but also according to the time and method of heating and cooling.

4. Owing to the displacement of the A_2 and A_1 points which occurs with varying silicon content, the positions of these two points are inverted when the silicon content exceeds 3·2 per cent. Si ; above this value the A_1 point is at a higher temperature than the A_2 point.

Microstructure.—Silicon tends to produce stable equilibrium conditions even in alloys of low carbon content ; graphite appears in these steels as soon as the silicon content is sufficient for any definite rate of cooling.

The normal steels containing less than 5 per cent. Si are pearlitic (Fig. 381, Pl. LXXII.) ; steels containing 5–7 per cent. Si consist of pearlite and graphite ; above 7 per cent. Si, pearlite no longer exists and only graphite is present. The microstructure is therefore independent of the carbon content. Definite compounds appear when sufficient silicon is present (Fig. 383, Pl. LXXII.).

The presence of silicon tends to increase the grain size. An interesting characteristic of the hardest silicon steels is the fact that polishing scratches which are not apparent before etching, are clearly visible after etching. Also, etching usually produces silica, which forms a film on the specimen and appears after drying as thin lines of polyhedral outline. These specimens must be washed with great care in water, alcohol, and in some cases, when necessary hydrofluoric acid.

Annealing produces a characteristic effect on the pearlitic steels (Figs. 382, 384, Pl. LXXII. ; Figs. 385, 386, Pl. LXXIII.) causing the liberation of graphite (temper carbon) even in steels of low carbon content ; thus a steel containing 0·28 per cent. C and 5·12 per cent. Si, after 24 hours annealing at 950° C., contains no trace of pearlite, the carbon appearing as specks of graphite.

The length of time that annealing must be continued to bring about the complete liberation of all the carbon into the graphitic form is lessened as—

1. The silicon content increases ;
2. The temperature is greater.

It should be noted that steels containing no pearlite and all graphite cannot be cemented (case hardened), since they do not absorb carbon.

Relation between the Microstructure and the Mechanical Properties.—Silicon steels cannot be forged when the silicon content exceeds

7 per cent. in the case of low carbon steels and 5 per cent. Si in steels containing 0·9 per cent. C.

Only steels free from graphite are used in practice. The ultimate strength is greater the higher the silicon content, and shows a decided increase above that of the ordinary carbon steels, but the brittleness increases in proportion to the silicon content.

Summary

Aluminium, boron, cobalt, tin, and titanium steels will not be considered in the present instance, as they are not in commercial use in France, except, perhaps, in certain special instances. In an introductory work of this nature it has not been found possible to give a complete outline of the even more complex quaternary steels; but a brief description of the nickel-chrome and chrome-tungsten steels (pp. 192–197) has been included, as these steels are of considerable industrial importance.

If the microstructures of commercially annealed ternary alloy steels are examined, the following constituents will be found: pearlite, ferrite, cementite, graphite, austenite, martensite, troostite, special carbides, and mixtures of two or more of these constituents will be observed.

The mixture of pearlite and ferrite is found in all kinds of special steels. This structure indicates that the total amount of the elements present, other than iron and carbon, cannot be very great; but does not necessarily indicate the presence of any special element.

Inversely, the existence after annealing of one of the following constituents: austenite, martensite, troostite, graphite, or the presence of a double carbide indicates a special steel. In certain instances it is possible by examination of the microstructure to identify the special element present, or at least to limit the number of possible elements present. Thus—

Graphite indicates silicon as the special element.

Carbides indicate the presence in comparatively large quantities, of one or more of the following elements: chromium, tungsten, molybdenum, vanadium.

Martensite indicates the presence of one or more of the following: nickel, manganese, chromium.

Austenite indicates a high content of nickel or manganese.

The simultaneous existence of martensite and carbide indicates a special steel, at least quaternary, containing: nickel (Ni-Cr, Ni-W, Ni-Mo, Ni-V steels), manganese (Mn-Cr, Mn-W, Mn-Mo, Mn-V steels), or chromium (Cr-W, Cr-Mo, Cr-V steels).

The simultaneous appearance of austenite and carbide indicates

a steel containing a high content of nickel or manganese together with chromium, tungsten, molybdenum, or vanadium.

The simultaneous occurrence of graphite and austenite is found in Ni-Si and Mn-Si steels of high nickel or manganese content containing a considerable quantity of silicon.

Special Cast Irons and Ferro-Alloys

The special cast irons are actually very little used in commerce, therefore the effect on the microstructure of a cast iron produced by the additions of special element will only be briefly considered.

As regards ferro-alloys, these are all at least ternary alloys consisting of iron, carbon and one or more of the following elements: manganese, silicon, chromium, tungsten, molybdenum, vanadium, etc. Since the constitution of the various binary alloys such as Fe-Cr, Fe-Mo, Fe-W is only known as regards their general outline, and also since these alloys frequently contain carbon and other elements in considerable proportions, it is obvious how premature it is to consider the microstructure of such alloys. It must not be overlooked that the examination of the chemical constitution must in every case precede the examination of the structure of an alloy or series of alloys. Without such preliminary examination the structural examination can merely consist of a collection of more or less decorative pictures or images accompanied by vague descriptions, which take no account of the varying conditions of manufacture and treatment or the presence of impurities which might modify or even completely change the form or appearance described as characteristic.

The only reliable information available relates to the existence of the definite compounds Fe_2Si and FeSi in the ferro-silicon series (Fig. 391, Pl. LXXIV., p. 185), and, in the other alloys, the presence of carbides (Figs. 393–396, Pl. LXXV., p. 204) under the headings of the respective alloy steels. The carbides often appear in bas-relief after polishing, and are very difficult to attack with etching reagents, even aqua regia; their distribution sometimes suggests that they may form part of a eutectic (Figs. 395–396, Pl. LXXV.).

Many of the ferro-alloys are brittle, friable, porous, and very difficult to polish. It may be mentioned in this connection, that with complex alloys of this nature microscopical examination cannot give the slightest information with regard to the chemical composition. Moreover, since such alloys are merely used as additions in the manufacture of other material, their mechanical properties are of no importance. Heat treatment is non-existent, and microscopical examination, from the practical point of view, adds no information to the results obtained from a complete chemical analysis. On the

other hand, it cannot be doubted that metallography will be found of great utility in the manufacture of ferro-alloys, more particularly to explain the different working qualities of these various alloys. Example: the marked advantages of ferro-chromes of low carbon content.

Effects produced by Special Elements on the Microstructure of Cast Irons.—From amongst the various modifications to the Fe-C equilibrium diagram caused by the introduction of definite amounts of special elements to ordinary cast irons, three typical examples will be chosen as most clearly affecting the microstructure.

1. **Effect on the Equilibrium Stability.**—Certain elements such as silicon assist the formation of stable equilibrium conditions, by which is meant the formation of graphite. Others, such as manganese, tend to the establishment of metastable equilibrium with the consequent formation of cementite. With ordinary cast irons, the conditions of cooling and annealing each produce their distinct effects, and it is possible, according to Wüst, by sufficiently slow cooling, to nullify the effect due to the manganese and thereby to obtain a grey cast iron. The separation of graphite depends mainly on the length of time the metal is retained at the eutectoid point.

The effects produced by silicon during annealing have been studied by numerous investigators; amongst others, Charpy and Grenet have shown that:

(*a*) The separation of graphite commences at a temperature which is lower the greater the silicon content, and that, once commenced, the separation continues at temperatures even lower than the commencing temperature.

(*b*) At any constant temperature the rate of separation of the graphite increases with this temperature and also with the silicon content.

(*c*) Also, and this is very important, the final condition depends only on the amount of carbon remaining in solution. The silicon merely serves to lessen the time required to attain this equilibrium.

The silicon therefore acts as a *catalyser*, increasing the rate of decomposition of the carbide of iron during annealing and inducing and assisting the formation of stable equilibrium conditions. This effect occurs even with alloys of low carbon content, as already illustrated in the case of silicon steels. According to Wüst, the separation of graphite is assisted by both tin and phosphorus, but the effect of the latter element is not appreciable below 2·5–3·0 per cent. P. Nickel produces a similar effect. Inversely, chromium acts in a similar manner to manganese and prevents the separation of graphite: 1·5 per cent. Cr, even when 2 per cent. Si is present, is sufficient to entirely prevent the separation of graphite (Goerens

and Stadeler). Sulphur opposes the separation of graphite in a similar manner (Wüst).

As stated by Bénédicks and one of the authors,[1] the elements which form stable carbides hinder the separation of graphite; inversely, those which form solid solutions tend to assist the separation of graphite. But it is possible to explain the different effects of the elements in a very simple manner, as suggested by Osmond and one of the authors.[2] The lines E*a* and SE′ of the combined equilibrium diagrams (Fig. 218, p. 130), indicating respectively the separation of graphite and cementite being adjacent for iron-carbon alloys containing no other elements, it is probable that the presence

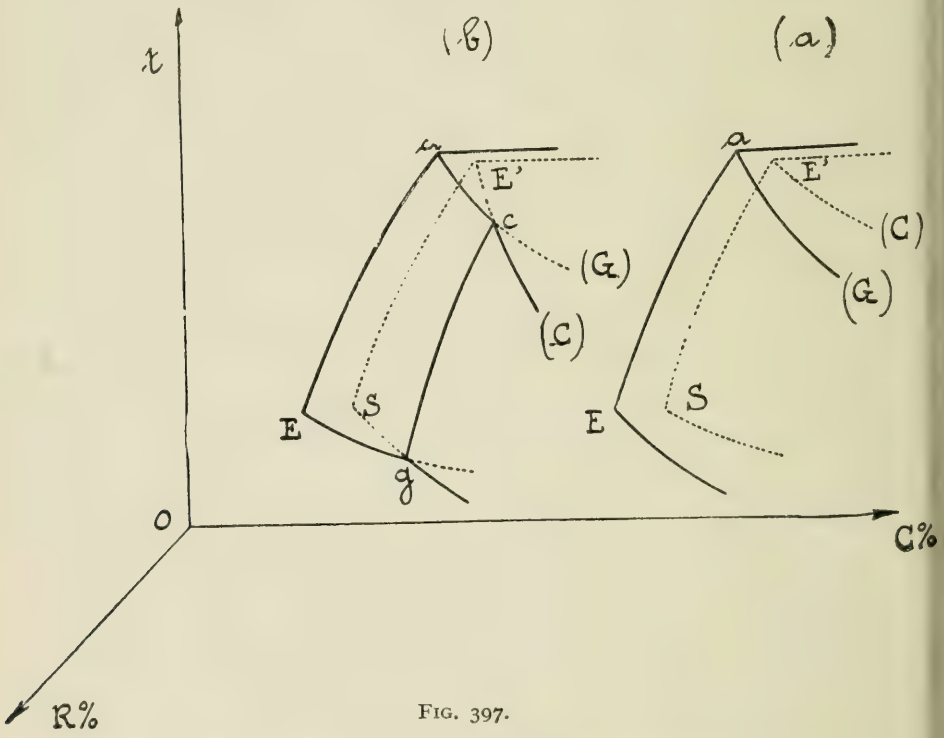


FIG. 397.

of silicon tends to separate the lines, whilst manganese tends to bring them closer together, and, at a certain manganese content, causes the line SE′ to pass above the line E*a*. It is then the ferrite-cementite system which is stable and the ferrite-graphite system which is labile or metastable.

This interpretation may be presented graphically in the following manner (Fig. 397): if the equilibrium of a system consisting of iron, carbon, and a third element R is considered, the separation of

[1] Guillet, "Les Fontes au nickel et les Fontes au manganese" (*Revue de Met.*, vol. v. p. 306, 1908).

[2] Portevin, "Etat actuel des théories de l'equilibre du système fer-carbone" (*Revue de Met.*, vol. iv. p. 1003, 1907).

graphite or cementite from the solid solution Fe-C-R will be shown, as a function of the temperature, as two surfaces (G) and (S) of which the intersections with the plane *to*C correspond exactly with the curves *a*E and E'S of the diagram (Fig. 397). These surfaces may either cut each other as in *b* (Fig. 397), or may separate further and further apart as in *a* (Fig. 397). In the first case, above a certain content of the element R, it is the cementite which becomes the stable form, and graphite is then the labile condition; whereas in the second case the graphite remains the stable form as the content of the special element R increases. It may happen even in the first case, according to the slope of the curve *cg* in relation to the plan *to*C (the curve *cg* marking the intersection of the surfaces (G) and (C)), that there may be certain contents of R at which graphite will be the stable form at high temperatures and cementite the stable form at low temperatures (in such a case, for that content of R, the diagram will be identical to the equilibrium diagram originally plotted by Roozeboom), and the inverse may also occur.

2. **Displacement of the Eutectic Point in the Case of the Labile System (Cementite).**—This displacement involves a consequent alteration of the eutectic temperature and eutectic composition. Actually, the degrees of freedom being increased by unity, the eutectic temperature is replaced by a eutectic interval and, what is more important, the eutectic solidification may be completed, if the content of the special element is sufficiently high, by the formation of a ternary eutectic.

Several examples may be quoted :

(*a*) Manganese displaces the eutectic content (16 per cent. Mn lowers the eutectic carbon content 0·15 per cent. C according to Wüst) ; it also lowers the temperature of solidification, but the results available do not agree (Wüst, Coe).

(*b*) Chromium displaces the eutectic composition in a similar manner ; an alloy containing 5 per cent. Cr and 4·7 per cent. C may be regarded as the eutectic (Goerens and Stadeler).

(*c*) Sulphur lowers the eutectic temperature and tends to the formation of a ternary eutectic cementite—sulphide of iron—pearlite (Donald M. Levy).

(*d*) Phosphorus lowers the eutectic solidification point and forms a ternary eutectic Fe_3C-Fe_3P—solid solution (Wüst), of which the solidification point is 953° C. and the composition : P = 6·89 per cent., C = 1·96 per cent. (Goerens and Dobbelstein).

3. **Effect on the Critical Point (Eutectoid Point of Formation of Pearlite** $A_{3,2,1}$**).**—This effect has been considered in the case of the special steels and, as regards the microstructure, it has been shown that the addition of elements such as Ni and Mn, other

conditions being constant, bring about the change from pearlite to martensite and then to austenite. Figs. 309, 310, Pl. LVII. (p. 152), are typical examples.

Nickel-Chrome Steels

Critical Points or Transformation Points.—It has been shown that, within certain limits, the addition of nickel depresses the transformation point on heating, which is, as a general rule, adjacent to the reversible transformation equilibrium temperature, and also increases the interval between the transformation temperatures on heating and cooling. Thus it operates simultaneously by depressing the equilibrium transformation temperature and increasing the hysteresis effect, which is sometimes termed the interference effect. Again, it has been shown that the presence of chromium produces but little effect on the transformation points (heating), but produces a considerable hysteresis effect. The combined simultaneous effect produced by the addition of both these elements, nickel and chromium, will therefore consist of a considerable depression of the transformation point on cooling, even when only small amounts of these elements are present. Thus there will be but slight differences in chemical composition between the steels in which the transformation on cooling occurs at 600° C. and those in which it occurs at 300° C. : 1 per cent. Ni and 1 per cent. Cr (Grenet).

Inversely, the position of the transformation point on heating will be almost entirely dependent on the nickel content.

The nickel-chrome steels may therefore be classified into three main categories [1] : those in which the transformation point on cooling is not far removed (100–125° C.) from the transformation point on heating (pearlitic steels) ; those in which the interval increases proportionally to the chromium content (martensitic steels) ; and finally a third category, all the alloys of which have approximately the same interval and in which the effect produced by chromium is but little evident (carbide steels). Thus, if chromium is added to a nickel steel, there will be a depression of the transformation point on cooling, and, under certain conditions, this depression may be very sudden; it is only necessary to add 1·7 per cent. Cr to a 4 per cent. nickel steel to depress the transformation temperature from 600° to 200° C., after which further additions operate very slowly (Grenet). It should be noted that the addition of chromium is also able to bring about the splitting up of the transformation point on cooling. It is evident that the rate of cooling is also a factor under these conditions ; thus steels containing sufficient carbon and sufficient chromium (above 1·5 per cent. Cr) may show a transformation either at 600° C. if the rate of cooling is very slow,

[1] Guillet, *C. R.*, 158, 412, 1914.

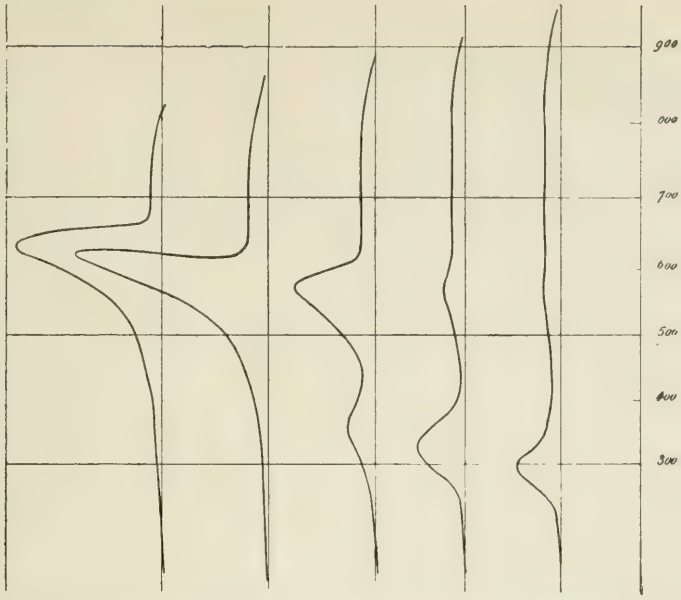


FIG. 398.—Cooling curves (differential method), showing the influence of the heating temperature.

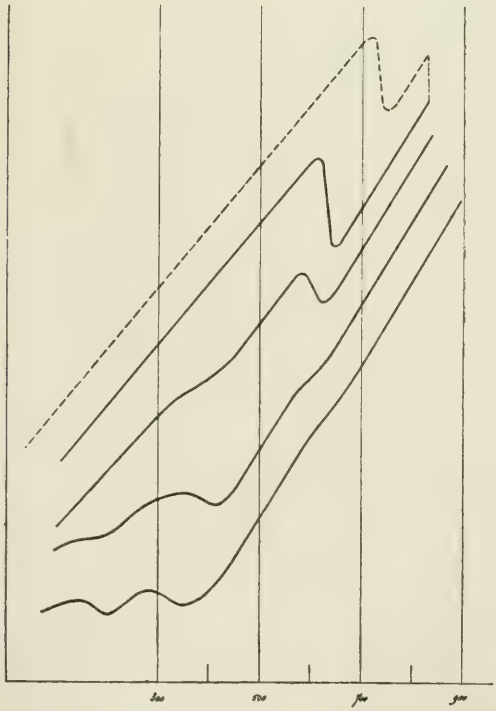


FIG. 399.—Dilatation curves on cooling, showing the influence of the heating temperature.

or at 200° C. if the cooling is more rapid; but this transformation cannot occur within the temperature range between 200° and 600° C. (Grenet). But the maximum heating temperature produces an even greater effect than the rate of cooling, as already shown in several preceding instances. The curves, Figs. 398, 399 (Chevenard), clearly show this effect in the case of a steel containing approximately 2·5 per cent. Ni and 1·5 per cent. Cr; as with the tungsten and molybdenum steels, above a certain temperature value or "depression temperature," the transformation point on cooling, which was at first slightly depressed, lessens in intensity and a further anomaly in the curves appears between 400° and 300° C.; two critical points appear, and if the temperature is still further raised, the upper point decreases and disappears whilst the lower point increases in size.[1]

Microstructure.—It has been shown that on the addition of increasing amounts of nickel to carbon steels, such steels pass from the pearlitic to the martensitic and finally to the austenitic condition; and that by similar additions of chromium, carbon steels change from the pearlitic to the martensitic condition, and finally appear as double carbide steels. The microstructure of nickel-chrome steels will therefore be martensitic and austenitic, owing to the considerable depression of the transformation point, on cooling, previously mentioned. The double carbide constituent will also appear when the chromium and carbon contents are sufficient to cause its formation; consequently:

(*a*) The addition of chromium to a pearlitic nickel steel will convert the steel to the martensitic condition; if the amount added is very small, only a diminution of the ferrite grain will be observed.

(*b*) The addition of chromium to a martensitic nickel steel is able to bring about the formation of double carbide and also to transform the martensite partially or entirely into austenite.

(*c*) The addition of chromium to an austenitic nickel steel induces the formation of carbide in the austenite when the chromium content is sufficient.

Finally, the following structure may be observed in the normal steels:—

1. Pearlite intermixed with ferrite or carbide.
2. Martensite.
3. Martensite with carbide.
4. Austenite.
5. Austenite and carbide.

The term "martensite" in this classification describes either the pure constituent or this constituent accompanied by ferrite or

[1] Ref. Portevin: "Sur les points de transformation des aciers nickel-chrome," *Revue de Met.*, Sept., 1917.

austenite. Quenching modifies the microstructure in a similar manner to that indicated in the case of nickel and chrome steels; it will be recalled that these steels exhibit a marked hysteresis effect, even at extremely slow rates of cooling, and that softening can only be achieved by tempering in the transformation area, but below the transformation temperature on heating.

Again, the structures of nickel-chrome steels of the same chemical composition and treatment may differ. The structure is then dependent on other factors, such as the thermal history when in the liquid state.[1]

Relation between the Microstructure and the Mechanical Properties.—The general statements mentioned in the case of nickel steels apply also in this instance; the present description will therefore be confined to structures not yet considered.

(*a*) Nickel-chrome steels containing martensite and carbide have practically the same properties as martensitic steels; but their ultimate strength and elastic limit decrease in proportion to the amount of carbon present.

(*b*) The nickel-chrome steels containing austenite and carbide have practically the same properties as the austenitic steels; but their elongation is less and their brittleness greater as the carbon content increases.

High-Speed Tool Steels

The term "high-speed steel" is usually applied to chrome and tungsten steels containing, as a general rule, from 0·2 per cent. to 1 per cent. C, from 7–18 per cent. or even 23 per cent. W, and from 1·5–3·0 per cent. and sometimes 8 per cent. Cr. These steels, in some instances, also contain 1 per cent. to 2 per cent. Mo and small quantities of vanadium.

The composition mentioned by Taylor is as follows:

C=0·8 W=17·81 Cr=5·95 V=0·32

That given by Le Chatelier:

C=0·5 W=12 Cr=3 Mo=1

An intermediate type may be given as:

C=0·5 W=18 Cr=5 V=0·2

Critical Points.—The transformation points are dependent on the temperatures to which the metal is heated in the case of the high-speed chrome-tungsten steels. This is shown in an extreme form by the expansion curves, Fig. 400,[2] in which a high-speed steel has been successively heated to 860°, 925°, and 1025° C. It may be

[1] Brès, *Revue de Met.*, vol. x. p. 797, 1914; Portevin, *Rev. de Met.*, vol. x. p. 808, 1914.

[2] The curves, shown diagrammatically, are those established by de Nolly.

mentioned that, as with steels containing tungsten, molybdenum, etc., there is an alteration of the transformation point above a certain temperature; the point at about 600°–700° C. then disappears and another point appears at 300°–400° C. Other factors also tend to produce this effect, but in a less appreciable manner, such as an increase in the rate of cooling, or longer time of heating (Böhler). Similarly, increasing the chromium or tungsten content assists this phenomenon.

In any case, there exists a range of temperature between 600° and 400° C. in which no critical point appears and in which the transformation is at least very slow and practically does not occur.

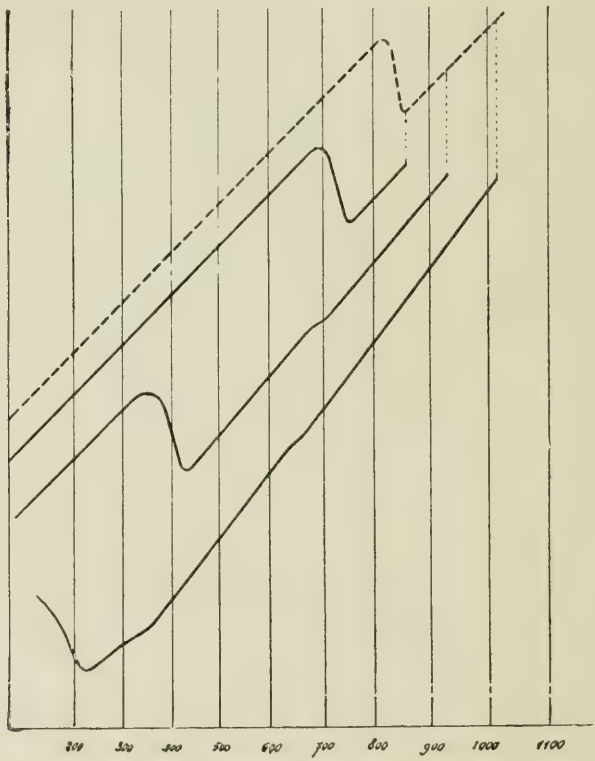


FIG. 400.

Two important conclusions are to be drawn from the examination of the effects produced by increasing heating temperature:

1. Above a certain heating temperature that may be termed "depression temperature," the transformation point on cooling, without any increase in the rate of cooling, will be found to correspond approximately with the atmospheric temperature: the steel is "self-hardening."

2. Within a temperature range extending from atmospheric temperature up to 600°, or a dull red heat, the transformation speed is so slow that tempering produces no effect; these steels may

therefore be used up to these temperatures without losing the properties they have acquired by quenching.

The commercial possibilities and uses of such steels are at once apparent.

Microstructure.—Chromium, tungsten, and molybdenum lower the eutectoid carbon content; the high-speed steels are therefore, in most cases, carbide steels. When the heating temperature exceeds the $Ac_{3\cdot2\cdot1}$ point, these carbides commence to pass into solid solution. Solution occurs slowly, but the speed increases with rise of temperature, the amount of the carbide dissolved being dependent on the temperature to which the steel is heated and the length of time heated. On cooling, the reverse conditions occur. The separation of the carbide does not readily take place, the position of the transformation points depending (neglecting the secondary effect due to the rate of cooling) on the concentrations of carbon and special elements in the solid solution, and therefore on the amount of carbon that has entered into solution during heating. But the solution of the carbide during heating occurs slowly and with great difficulty. Therefore, unless the steel is heated to extremely high temperatures, where the rate of diffusion is high, the solid solution with or without residual carbide will remain heterogeneous, the areas of high carbon concentration surrounding the residual carbide areas or replacing the areas previously occupied by carbide. During cooling, the areas of higher concentration behave differently to those of lower concentration, hence the frequent splitting up of the transformation point on cooling.[1]

By progressively increasing the heating temperature, Osmond has obtained the following series of results from the same specimen:

1. Sorbite and carbide (one recalescence).
2. Troostite and carbide (one recalescence).
3. Troostite and martensite (two recalescences).
4. Martensite and a mixture of martensite and austenite (only one recalescence recorded).

As a general rule, only one recalescence is found if the heating temperature does not exceed a temperature T_1, but slightly above the $Ac_{3\cdot2\cdot1}$ point, since the diffusion of free carbide is then practically negligible; it splits up on heating between T_1 and $T > T_2$, and again shows a single recalescence above T_2 when the distribution of the carbide has become homogeneous. Finally, the structure of high-speed steels will usually consist of carbide, the quantity of which is dependent on the composition and treatment, in a ground mass of sorbite, troostite or martensite. Quenching causes the disappearance of the cementite and the formation of martensite with or without troostite or austenite.

[1] Osmond, *Revue de Met.*, vol. i. p. 351, 1904.

CHAPTER V

INDUSTRIAL APPLICATIONS OF METALLOGRAPHY TO METALS AND ALLOYS OTHER THAN IRON AND STEEL

THE INDUSTRIAL METALS

BEFORE dealing with the application of metallography to the manufacture and utilisation of various alloys, it appears essential to devote several pages to the various industrial metals, their physical and mechanical properties, and more common impurities.

Microstructure of the Common Industrial Metals.—It has been shown (Chap. II., pp. 67–72) that during solidification the pure metals crystallise in the form of dendrites, which separate from the liquid and form, by mutual limitation, the grains of solidification or crystal grains.

The size of these grains depends, with any given metal, on the conditions of cooling. The peripheral zones of metals and alloys cast in ingot moulds (chills) are particularly likely to exhibit a columnar structure. Thermal and mechanical treatment and changes that occur on passing through the transformation points modify the crystalline structure in the manner previously described. But the pure metals and more generally the homogeneous solid solutions always possess a structure corresponding to a conglomerate of individual crystals or grains, the size of which is a direct result of all the operations to which the material has been subjected.

Only in rare instances is an industrial metal free from all impurity. It is therefore of primary importance to ascertain the effects produced by these impurities on the microstructure, and more particularly on the physical and mechanical properties of the metal.

Effect of Impurities on the Microstructure.—An impurity, in a metal, may behave in one of three ways :

1. Enter into solution in the metal, modifying the crystal grains to a greater or less extent.
2. Solidify and still maintain its chemical entity.
3. Form a special constituent.

The examination of the effect an impurity produces on the structure of a metal is equivalent to studying the equilibrium diagram of the metal and this impurity in the region of the pure

metal.[1] But it is necessary to add that usually several impurities are present, and their combined effect may considerably modify the result that might be expected from the examination of the effects produced by the single impurities. Thus it may happen that the addition of a substance to an alloy induces the solution of a third substance, or that two impurities separately soluble in the first metal in the solid state may form a definite compound when both are present. Very little reliable information has been obtained with regard to these effects.

Consider the case of a single impurity. If the impurity enters into solution in the metal, the diagram will show an inclined branch of the solidus, commencing from the melting-point of the pure metal. If the impurity solidifies and still retains its chemical isolation or forms a separate constituent, the solidus, adjacent to the pure metal, will consist of a horizontal touching the vertical at the melting point of the pure metal. Only by the thorough examination of the diagram will it be possible to decide whether solidification occurs in the form of the isolated impurity or as a separate constituent—compound or solid solution.

Impurities of Commercial Copper.—The following table (p. 200) gives a series of typical analysis of commercial copper obtained from Hollard's "Traité d'analyses." It will be seen that the chief impurities are: silver, gold, arsenic, antimony, nickel, cobalt, iron, lead, bismuth, and very rarely tin. Amongst these impurities:

1. Silver, gold, nickel, cobalt, tin, and iron are soluble within the limits found in commercial copper.

The diagram references are:

Silver-copper (Fig. 511, p. 254).

Gold-copper (Fig. 512, p. 255).

Nickel-copper (Fig. 488, p. 241).

Tin-copper (Fig. 437, p. 228).

Cobalt-copper (Fig. 401, p. 201).

Copper and cobalt form a solid solution containing up to 3 per cent. Co. This point has been found by conductivity and thermo-electric methods.

There is a very close resemblance between the copper-cobalt and the copper-iron alloys; at the copper end of the copper-iron series there exists a solid solution containing 3 per cent. iron.

Lead separates from copper even in the liquid state (see diagram, Fig. 494, p. 246). The diagrams are also given for the other impurities: arsenic, bismuth, and manganese (Figs. 405, 403, 404).

Copper and arsenic form solid solutions in which the arsenic

[1] In this connection the importance of the examination of the electrical properties in relation to the diagram may be noted.

Copper (Analyses by Hollard).

Brands of Copper.	Cu	Ag	Au	As	Sb	Sn	Ni + Co	Fe	Zn	Pb	Bi	
1. Chili.												
Urmeneta	97·668 96·979 99·915	0·0395 0·0369 0·0129	0·0016 0·0016	0·094 0·073 0·009	0·102 0·070 0·002	— — —	0·314 0·413 0·005	0·577 1·248 —	— — —	0·000 0·042 traces	0·034 0·053 —	
Lota	99·822 99·775	0·0243 0·0092	0·0007	— 0·016	0·038 0·004	— —	0·037 0·027	traces —	— —	0·029 traces	— traces	
Catémon	98·623	0·0849	0·0001	0·047	0·000	—	0·114	0·295	—	0·021	0·034	
2. Lake Superior.												
Calumet and Hecla	99·963	0·0272	—	0·009	0·000	—	0·000	0·004	—	traces		
Tamarac	99·741 99·862	0·1120 0·0455	—	0·037	0·013 0·004	— —	0·000 0·007	traces	0·000 —	0·000 traces	— —	
Quincy	99·844	0·0940	—	—	0·005	—	0.000	0·008	0·000	0·000	—	
Oscéola	99·898	0·0430	—	0·037	0·010	—	0·012	—	—	traces		
Oscéola	99·813	0·0480	—	0·033	0·088	—	0·008	0·002	—	0·000	0·010	
3. Boléo.												
Californian Peninsula ..	96·580 91·818 90·022	0·0192 0·0190	traces traces	0·039 0·028 0·041	0·054 0·018 0·006	0·106 0·164	0·311 0·419 0·967 0·900 1·130	0·955 4·420 5·232	0·653 0·700	0·172 0·006 0·233	0·000 0·000 0·015	S = 0·124 Mn = 0·124
4. United States.												
Electro Montana	99·835	0·0000	—	—	0·010	—	0·007	0·004	—	traces	—	
Arizona	99·731				0·096	—	0·053	0·017	—			
5. Bolivia.												
Corocoro	99·842	0·0000	—	—	0·027	—	0·039	0·008	—	0·000	—	
6. Australia.												
Wallaroo	99·610	—	—	0·002	0·074	—	0·236	0·000	—	0·000	0·040	
Colzar (electro)	99·947	—	—	0·008	0·026	—	0·009	0·006	—	0·000	0·004	
7. Japan.												
Sumitomo	99·806	0·0142	0·0004	0·009	0·020	—	0·046	0·006	—	0·000	0·003	
Furukawa	99·262	0·1002	traces	0·068	0·016	—	—	—	—	—	—	
Furukawa	98·996	0·1134	0·0002	0·022	0·018	—	—	—	—	—	—	
Kohnsen	98·224	0·0624	0·0024	0·062	0·088	—	—	—	—	—	—	
Yokohama	99·671	0·0472	0·0003	0·041	0·076	—	0·047	—	—	0·050	0·000	
Kitagawa	99·371	0·0238	0·0004	0·077	0·052	—	0·066	—	—	0·018	—	
Hibira	98·856	0·0150	0·0016	0·032	traces	—	0·080	0·038	—	0·026	traces	
Mitsu-Bishi (electro) ..	99·983	—	—	0·000	0·012	—	—	traces	—	0·000	traces	
Segava-Orokawa	98·589	0·0282	traces	0·072	0·030	—	0·020	0·038	—	0·043	traces	

The principal brands of copper used in commerce are (in order of value):
Fine copper: 1. Electro as cathodes or ingots. 2. Best Rio, Cape, Calumet, Champion, Baltu.
Scrap copper: 1. Locomotive fire boxes. 2. Wire. 3. New scrap, clippings, etc. 4. Cooking vessels. 5. Scrap metal. 6. Tinned scrap.

content may be as much as 3 per cent. As. The η constituent, which is the definite compound Cu_3As (28·3 per cent. As), then appears. Bengough and Hill [2] have shown that prolonged annealing brings about the formation of this constituent even when the arsenic content is less than 3 per cent As.

The constitutional diagram of the antimony-copper alloys has been investigated by Henry Le Chatelier, Baykoff, Parravano, and Viviani. The latest diagram, that constructed by Carpenter (1913).

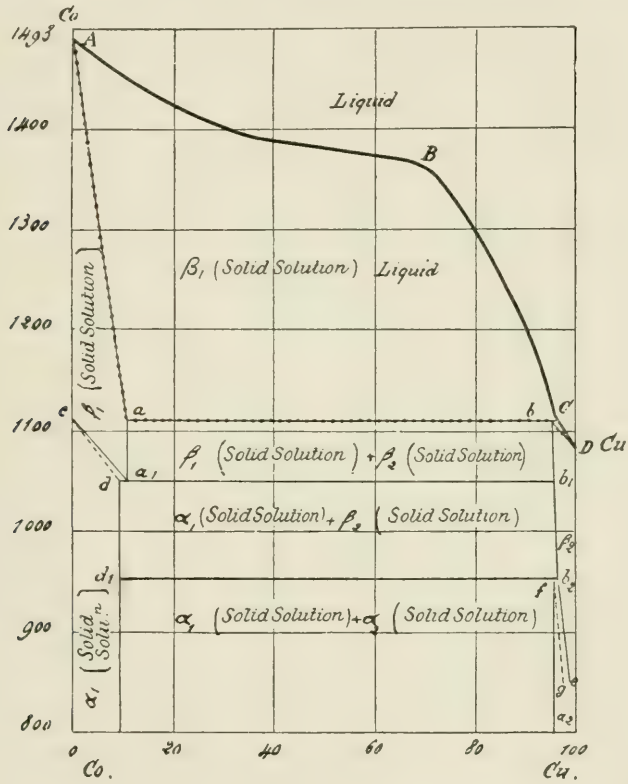


FIG. 401.—Copper-cobalt diagram (Sahmen).

shows the antimony-copper solid solution to contain up to 4 per cent. Sb.

The copper-bismuth alloys, investigated by one of the authors,[1] show no miscibility in the solid state. Bismuth remains isolated within the copper, and only very small quantities (0·02 per cent.) are required to entirely destroy the hot working properties of the metal.

Copper oxidises during melting, and it is frequently necessary to deoxidise the metal just before casting. This operation

[1] *Inst. of Metals*, June, 1910, iii. 34.
[2] Portevin, *Rev. de Met.*, vol. iv. p. 1077, 1907.

is performed by adding one of the following: phosphorus in the form of phosphor-copper, silicon and manganese generally in the form of alloys, magnesium or cadmium in the metallic state.

The sections of these diagrams required in the examination of the impurities of commercial copper are given (Figs. 403–408).

It will be noted that manganese enters into solid solution with copper, the two metals being entirely miscible in the solid state;

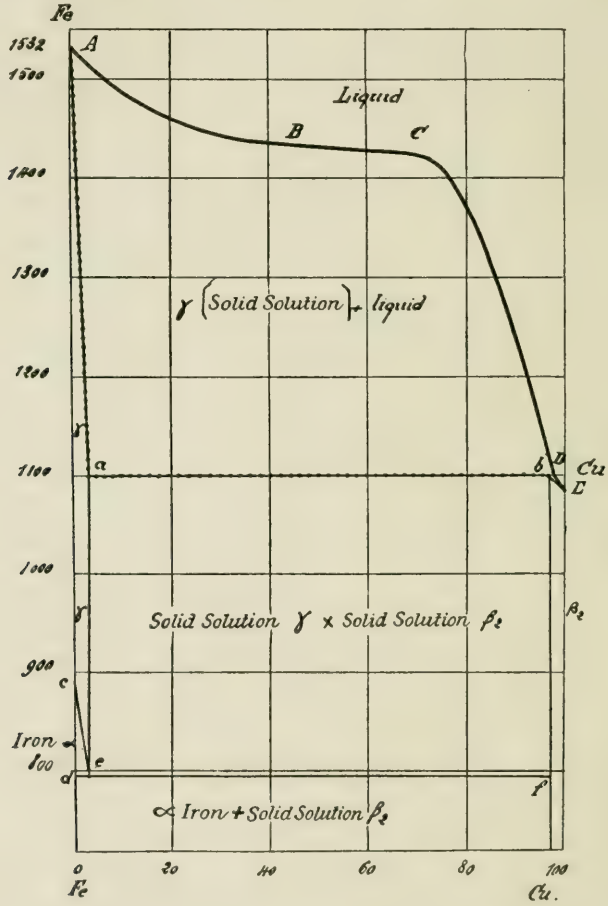


FIG. 402.—Iron-copper diagram (Sahmen).

silicon forms a solid solution with copper, the maximum concentration of which is 4·5 per cent. Si.

Phosphorus forms a solid solution with copper, the maximum content of phosphorus in this solution not exceeding 0·2 per cent.; above this phosphorus content, the compound Cu_3P forms a eutectic with copper. The eutectic point corresponds to a phosphorus content of 8·16 per cent. at a temperature of 707° C. The compound Cu_3P contains 14·1 per cent. phosphorus.

Magnesium does not form a solid solution, but separates as a

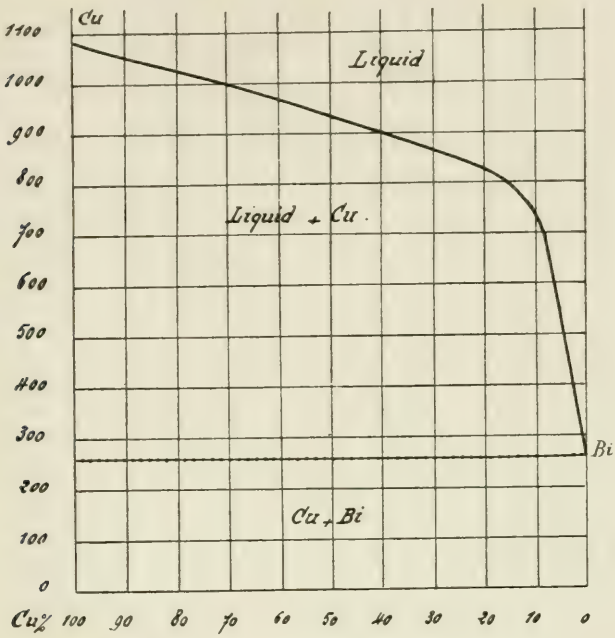


FIG. 403.—Copper-bismuth diagram (Portevin).

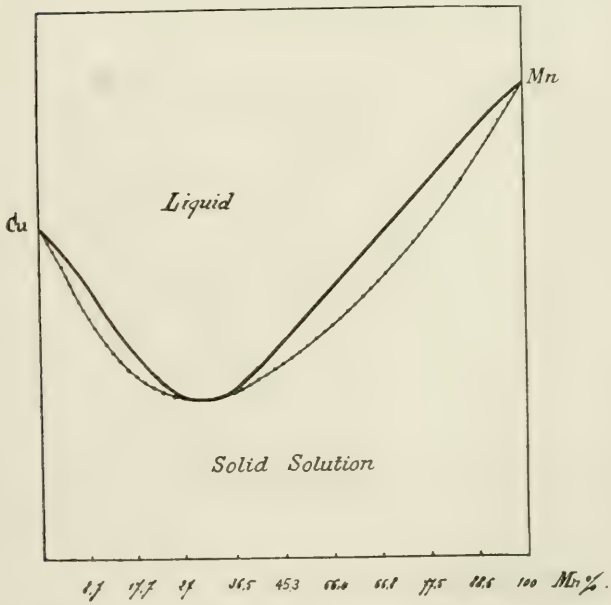


FIG. 404.—Manganese-copper diagram (Zemczuzny, Urasoff and Rykowskoff).

compound Cu_2Mg, which forms a eutectic with copper. This

explains the restricted use of magnesium as a deoxidiser, the effect produced by this impurity on the mechanical properties of copper being considered later.[1]

Cadmium is insoluble in copper in the solid state.

Lastly, an impurity to which it is impossible to devote too much attention, oxygen, which combines with copper to form an oxide of copper,

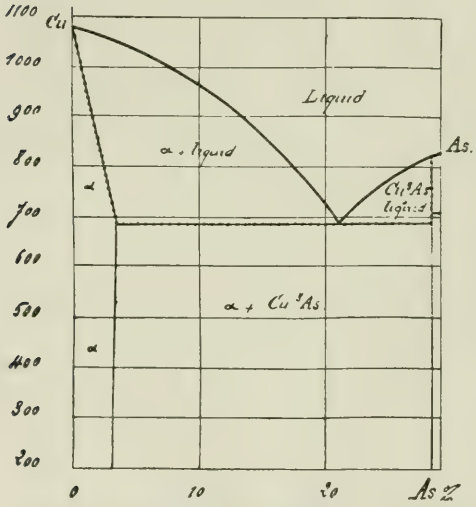


FIG. 405.—Copper-arsenic diagram (Bengough and Hill).

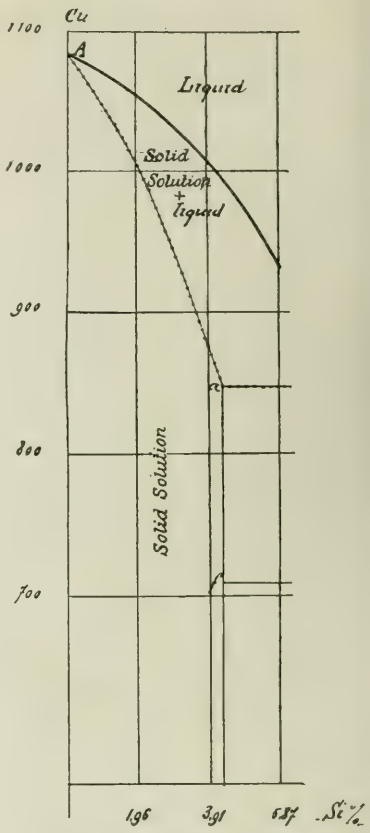


FIG. 407.—Section of copper-silicon diagram (Doernickel).

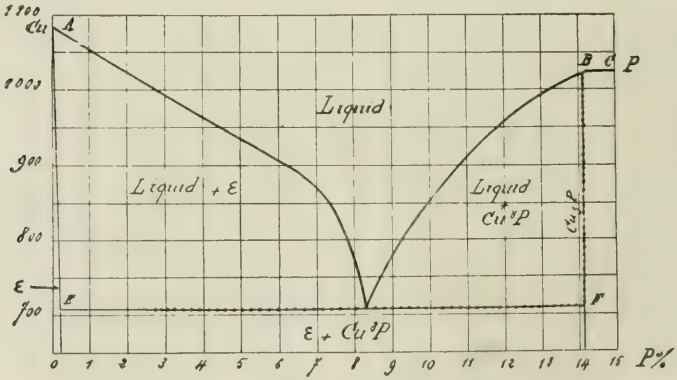


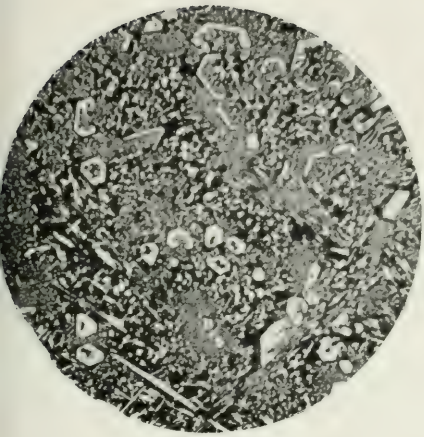
FIG. 406.—Copper-phosphorus diagram (Heyn and Bauer).

Cu_2O, that is soluble in molten copper and insoluble in solid

[1] Reference may also be made to Huser's experiments, *Metall. und Erz.*, vol. x. p. 479, 1913; *Revue de Met.*, vol. xi. *cont.*, p. 105, 1914.

FERRO-ALLOYS (*cont.*).

Ferro-chromes.



(C = 5; Cr = 65.)
FIG. 393.—Crystals of carbide + eutectic.
(× 50.)

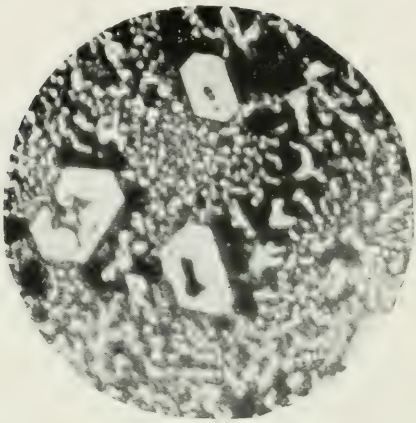
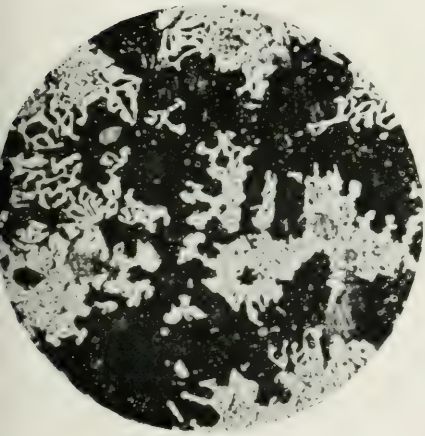
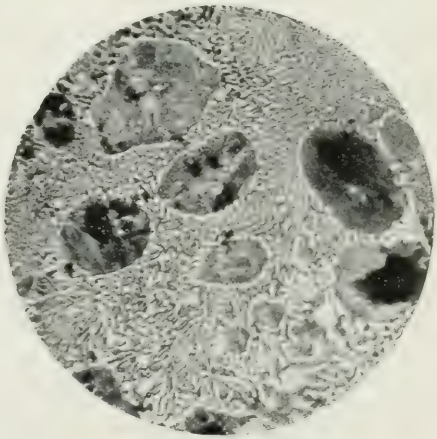


FIG. 394.—The same as Fig. 393.
(× 200.)

Etchant: Aqua regia.



(C = 1·85; Cr = 67.)
FIG. 395.—Ferro-chrome.
Etchant: Aqua regia.
(× 50.)



(C = 1·36; Cr = 40·2.)
FIG. 396.—Annealed at 1300° C. for 4 hours.
Carbide eutectic.
Etchant: Aqua regia.
(× 200.)

COPPER AND OXIDE OF COPPER.

(GIRAUD.)

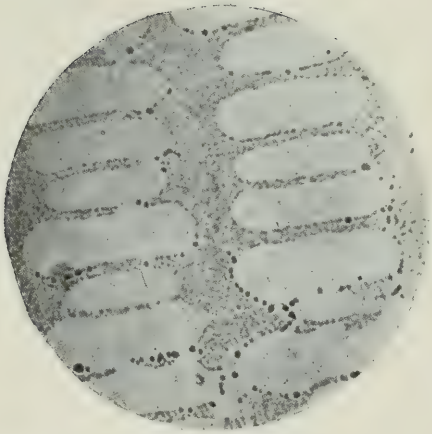


FIG. 409.—Copper and eutectic of Cu—Cu_2O.

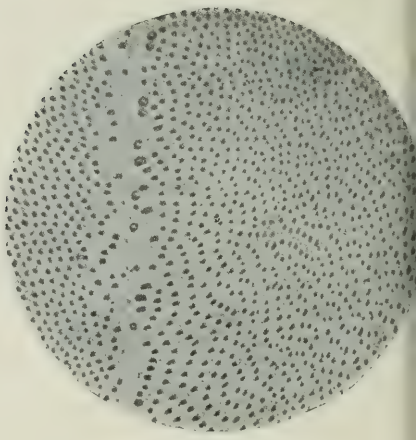


FIG. 410.—Eutectic Cu —Cu_2O.

FIG. 411.—Copper and oxide of copper without eutectic.

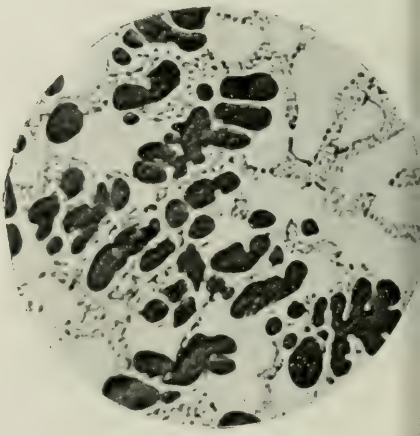


FIG. 412.—Copper, oxide of copper and eutect Cu—Cu_2O

copper. This oxide of copper may be seen under the microscope before etching, and possesses a characteristic sky-blue colour. According to results obtained by Heyn and Bauer, it forms a eutectic having an oxygen content of 3·5 per cent. O_2. Dejean gives the eutectic temperature as 20–25° C. below the melting point of pure copper. The phenomenon of surfusion may occur as shown by Giraud (*Revue de Met.*, vol. ii. pp. 297, 1905). Characteristic structures of copper oxide are illustrated in Pl. LXXV. *cont.* Micro-

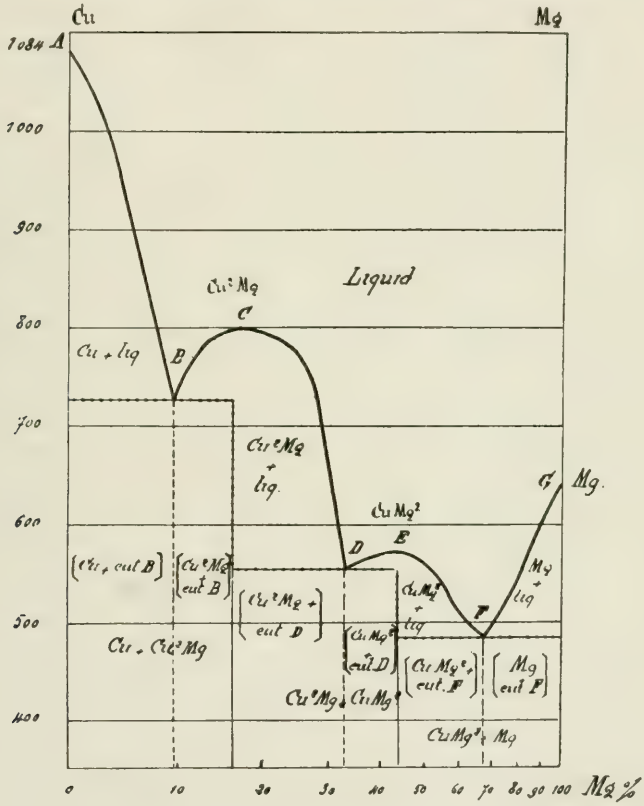


FIG. 408.—Copper-magnesium diagram (Sahmen).

scopical examination enables the presence of copper oxide in pure copper to be immediately detected.

Impurities of Commercial Tin.—The table on p. 208 gives a series of typical analyses of commercial tin (Hollard and Bertiaux).

It will be observed that the principal impurities are: antimony, lead, arsenic, copper, and bismuth. Antimony forms a solid solution with tin containing a maximum of approximately 8 per cent. Sb (see diagram, Fig. 495, p. 247).

Lead forms solid solutions with tin up to a maximum of 7 per cent. Pb (see diagram, Fig. 493, p. 245).

Zinc.

Brands.	Zn	Pb	Fe	Cd	Sn	Cu	Ag	As
Campredon	98·570	1·370	0·029	0·053	0·024	—	—	—
,, ...	96·249	3·610	0·064	0·077	traces	—	—	—
,, ...	97·780	2·150	0·015	0·051	—	—	—	—
,, ...	99·108	0·670	0·019	traces	—	—	—	—
,, ...	95·761	4·220	0·019	traces	—	—	—	—
,, ...	98·120	1·730	0·114	0·036	—	—	—	—
Schneider and Peterson	—	1·4483	0·028	0·0245	—	0·0002	0·0017	traces
,, ,, ...	—	1·7772	0·0288	—	—	—	traces	—
,, ,, ...	—	1·1921	0·023	—	—	0·0002	0·0007	—
,, ,, ...	—	0·633	0·032	0·054	—	traces	traces	—
Hollard and Bertiaux, Sardaigne	—	0·125	0·016	0·000	—	0·010	—	—
,, ,, Campine (Holland)	—	0·856	0·024	0·000	—	0·010	—	—
,, ,, Vieille-Montagne (crude)	—	0·540	0·049	traces	—	0·000	—	—
,, ,, ,, (brass)	—	1·070	0·016	0·010	—	0·000	—	—
,, ,, ,, (extra pure) ..	—	0·192	0·049	traces	—	0·002	—	—
,, ,, Zinc electro	—	0·156	0·008	—	—	traces	—	—
,, ,, ,, ...	—	0·104	0·016	traces	—	traces	—	—
,, ,, ,, ...	—	0·149	0·038	traces	—	0·000	—	—
,, ,, Hohenlohe (Silesia)	—	1·154	0·033	traces	—	0·000	—	—
,, ,, Refinado (Cie Asturienne)	—	0·180	0·015	0·000	—	0·000	—	—
,, ,, Côte-d'Or	—	1·450	0·063	traces	—	0·000	—	—

The Société de la Vieille-Montagne markets many brands of zinc, the principal being :

1. Extra pure A containing less than 0·10 per cent. impurities.
2. Extra pure B ,, ,, 0·30 per cent. ,,
3. Fonte d'Art M 11 ,, ,, 0·75 per cent. ,,
4. Fine brass ,, ,, 1·30 per cent. ,, (No. 1. commercial).
5. Ordinary brass ,, ,, 2·0 per cent. ,, (No. 2 ,,).

LEAD.

Brands.	Cu	As	Sb	Sn	Ni + Co + Zn	Fe	Ag	Bi	Mn	S
Hollard and Bertiaux, Sardinia	0·013	0·007	0·026	0·000	0·013	0·006	—	0·015	—	—
,, ,, ,, ...	0·000	0·118	0·000	0·000	0·010	0·015	0·0009	0·030	0·000	—
,, ,, ,, ...	0·010	0·004	0·018	0·000	0·025	0·003	traces	0·012	0·000	0·018
,, ,, Auvergne	0·005	0·002	0·028	—	0·028	0·011	—	0·028	0·000	—
,, ,, Penaroya (Spain) ..	traces	—	0·003	0·000	0·005	0·012	—	0·091	—	—
,, ,, Hoboken-les-Anvers ..	0·000	0·000	0·008	0·021	0·007	0·014	0·0003	0·120	—	—
,, ,, ...	0·040	0·007	0·010	0·000	0·016	0·010	traces	traces	0·000	—
,, ,, ...	traces	0·024	0·008	0·000	0·008	0·010	0·0015	0·030	—	—
,, ,, Laurium	0·133	—	0·681	0·000	traces	traces	1·9550	0·012	—	—
,, ,, De-silvered lead ..	0·003	0·005	0·036	0·090	0·100	0·064	—	0·014	—	—
,, ,, ...	traces	—	traces	—	0·012	traces	traces	0·480	—	—
,, ,, ...	0·057	—	—	0·000	traces	0·002	traces	traces	—	—
,, ,, Perth Amboye ..	traces	—	—	0·000	traces	0·003	traces	0·004	—	—
Jagnaux	0·048	traces	0·108	—	—	0·084	—	—	—	0·174
,, ...	0·016	0·016	0·084	—	—	0·007	—	—	—	0·010
Reich	0·250	0·160	traces	—	—	0·050	0·53	—	—	—
Keith	0·000	traces	traces	—	—	0·000	0·00007	—	—	—

Copper does not form solid solutions.

Bismuth produces similar results to antimony (Fig. 497, p. 249).

COMMERCIAL TIN.

Description.	Cu	As	Sb	Ni + Co	Fe	Zn	Pb	Bi
German tin	0·480	0·079	0·545	—	—	—	0·000	0·060
Swiss tin	—	0·022	1·174	—	—	—	0·498	0·580
Tonkin tin	0·000	0·034	0·110	0·028	0·040	—	0·076	—
Chinese tin	0·040	0·118	0·044	—	0·037	—	0·833	—
Detroit tin	0·030	0·033	0·000	0·014	0·008	0·000	0·081	—

The principal brands of tin used in commerce are as follows (in order of output): 1. Banca. 2. Billiton. 3. English. 4. Chinese tin and 99 per cent. tin. 5. 98 per cent. tin. 6. 97 per cent. tin. 7. 90 per cent. tin, and Bolivian tin.

Impurities of Commercial Zinc.—The table, p. 206, gives typical analyses of various brands of commercial zinc.

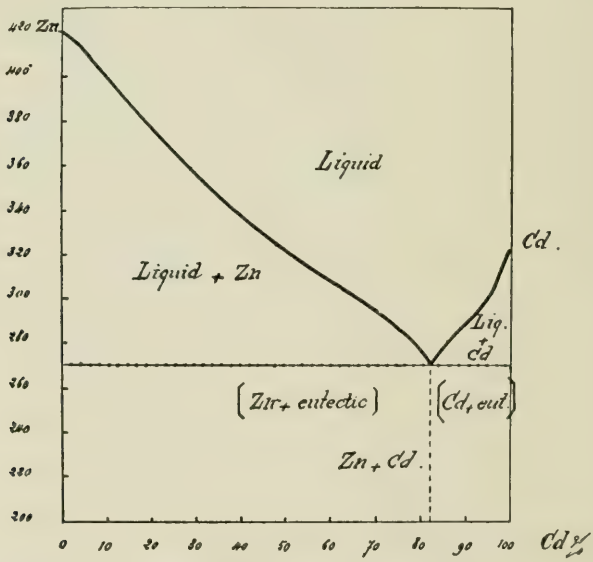


FIG. 413.—Zinc-cadmium diagram (Hindrichs).

Lead, iron, and cadmium constitute the chief impurities.

Lead and zinc are completely non-miscible in the solid state but are partially miscible in the molten condition.

Iron forms a series of solid solutions with zinc, but the maximum content of iron is very low and has not been accurately determined. It is a function of the rate of cooling and even under the most favourable conditions does not exceed 0·7 per cent. Fe. Above this value there is a second solid solution containing the compound $FeZn_7$.

Cadmium separates from zinc in the free state forming a eutectic as shown in the diagram (Fig. 413).

Impurities of Commercial Lead.—The table, p. 207, gives typical analyses of various brands of commercial lead and shows that the principal impurities are: arsenic, bismuth, iron, antimony, and silver.

Bismuth separates as a solid solution (see diagram, Fig. 496, p. 248).

Antimony separates in the free state (see diagram, Fig. 492, p. 244).

Silver and lead have a similar type of diagram, and this fact has been of considerable importance in the metallurgy of lead, since it has formed the basis of the Pattinson process for the desilverisation of lead. This process is now little used except for treating argentiferous lead containing bismuth.

Thus silver separates from lead in the free state.

Lead and iron are not miscible in the molten or solid state.

Impurities of Commercial Nickel.—The following table gives typical analyses (Hollard) of various brands of commercial nickel.

FIG. 414.—Section of nickel-carbon diagram.

The principal impurities are: cobalt, copper, iron, and graphite. The first three impurities are completely soluble in the solid state.

Graphite, which is soluble in nickel in the molten state, separates from the alloys rich in nickel during solidification; this is not apparent from the diagram (Fig. 414), which is incomplete.

Nickel is frequently refined before rolling by the addition of magnesium or manganese.

Nickel does not form a solid solution with magnesium. It forms a compound Ni_2Mg which separates as a eutectic (Ni-Ni_2Mg). The magnetic transformation point of nickel is therefore not affected by the addition of magnesium (Fig. 415).

Nickel and manganese form a complete series of solid solutions as shown by the diagram (Fig. 416). The alloys of mean concentration show a transformation in the solid state (Dourdine).

Impurities of Commercial Aluminium.—The table p. 212, gives several typical analyses of commercial aluminium.

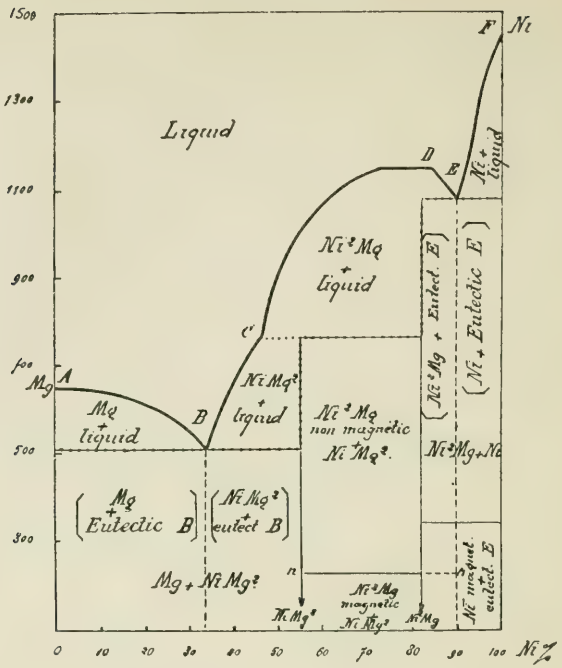


FIG. 415.—Nickel-magnesium diagram (Voss).

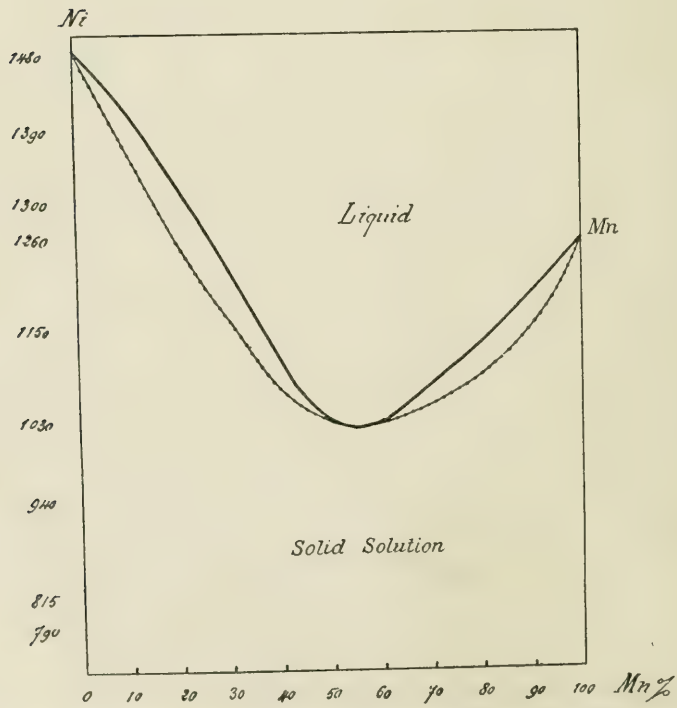


FIG. 416.—Nickel-manganese diagram (Zemczuzny, Urasoff and Rykowskoff).

NICKEL (Analyses by Hollard).

Brands of Nickel.	Cu	As	Sb	Sn	Co	Fe	Zn	Pb	S	MgO	CaO	SiO	Graphite	C total	Ni + Co
1. COMMERCIAL NICKEL.															
Grain nickel (American) ..	0·116	0·028	0·034	—	—	0·497	0·000	0·010	—	0·307	0·262	1·169		—	—
Grain nickel	0·126	0·073	0·040	0·038	0·706	0·626	—	0·072	—	—	—	—	—	—	—
,, ...	0·156	0·029	0·025	0·096	0·525	0·497	—	5·015	—	—	—	—	—	—	—
Silesian nickel	0·334	0·008	—	—	0·190	0·391	—	0·000	0·000	—	—	0·858		—	—
Cube nickel	0·336	0·008	0·012	—	—	0·644	0·000	0·003	—	0·000	0·104	0·732		—	—
,, ,, ...	0·062	0·006	0·014	—	1·552	0·253	0·000	0·000	0·022	0·022	0·071	0·467	0·147	0·289	—
2. REFINED NICKEL.															
French coinage, 1903	0·102	—	—	—	1·587	0·254	—	—	0·039	0·000	0·000	0·254	—	—	99·437
English nickel	0·058	—	—	—	0·462	0·647	—	0·000	0·015	—	—	0·184	—	—	—
Electro nickel	0·030	0·008	—	—	1·400	0·436	—	0·000	0·000	—	—	0·017		—	—
,, ,, ...	0·040	0·006	—	—	0·710	0·046	—	0·000	0·000	—	—	—	—	—	—
,, ,, ...	0·026	—	—	—	—	5·058	—	—	0·005	0·000	0·000	0·031	—	—	—
Nickel	0·104	0·011	0·024	—	1·449	0·311	0·000	0·000	0·010	0·000	0·005	0·222	—	—	97·857 + 1·449
,, ...	0·392	0·015	0·060	—	—	0·514	—	—	0·076	—	—	0·900	—	—	

ALUMINIUM.

Brand.	Mark.	C	Si	S	P	Pb	Cu	Fe	Cr	Na	Al	As	Mn	Zn	Ni+Co
Campredon	—	0·2000	0·4245	0·0068	0·0220	0·2040	0·9385	0·6840	—	0·1800	—	—	—	—	—
,,	—	0·1000	0·1465	0·0027	0·0290	0·0736	0·4790	0·5860	—	0·1400	—	—	—	—	—
,,	—	0·4450	0·0933	traces	0·0007	0·3074	0·5710	0·6840	0·5150	0·1597	—	—	—	—	—
,,	—	0·4750	0·0280	0·0110	0·0200	0·1814	0·5750	0·6500	0·5836	0·1600	—	—	—	—	—
,,	—	0·1600	0·0840	0·0220	traces	0·5028	0·2719	0·9260	—	0·1790	—	—	—	—	—
,,	—	0·0500	0·1979	0·0038	0·0050	0·6270	0·9390	1·2320	0·3752	0·0200	—	—	—	—	—
Moissan	Pittsburg 1898	0·41	0·15	néant	—	—	0·35	0·27	—	0·10	98·82	traces	—	—	—
,,	Neuhausen 1896	0·30	1·94	—	—	—	—	1·08	—	—	96·12	—	—	—	—
,,	Aluminium 1897	—	0·05	—	—	—	traces	0·19	—	—	99·80	—	—	—	—
,,	—	—	0·03	—	—	—	traces	0·32	—	—	99·18	—	—	—	—
Hollard and Bertiaux	—	—	0·221	—	—	0·000	0·036	0·109	—	—	—	—	traces	0·562	0·018
,, ,,	—	—	—	—	—	—	0·150	0·661	—	—	—	—	0·040	0·000	—
,, ,,	—	—	—	—	—	0·000	0·578	0·913	—	—	—	—	—	0·000	0·757
,, ,,	—	—	traces	—	—	—	0·000	0·179	—	—	—	—	—	0·000	traces
,, ,,	—	—	0·109	—	—	0·000	0·036	0·400	—	—	—	—	traces	—	0·130[1]
,, ,,	—	—	0·377	—	—	0·123	0·848	0·544	—	—	—	—	0·000	0·000	0·040

[1] This figure gives Ni + Co + Zn.

Silicon, copper, and iron are the principal impurities and also carbon which is insoluble in aluminium.

Copper forms a solid solution (see diagram Fig. 467, p. 237).

Iron does not form any solid solution with aluminium, as shown by the diagram (Fig. 417). There is a eutectic closely approximating to pure aluminium composed of aluminium and the compound $FeAl_3$. It may therefore be considered that iron separates in the form of $FeAl_3$.

The aluminium-silicon diagram shows the existence of a eutectic with a silicon content of 10 per cent. Si and a eutectic temperature of 580° C. If

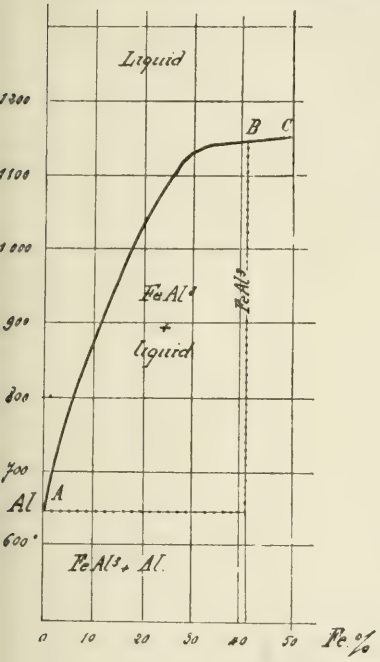


FIG. 417.—Section of aluminium-iron diagram (Gwyer).

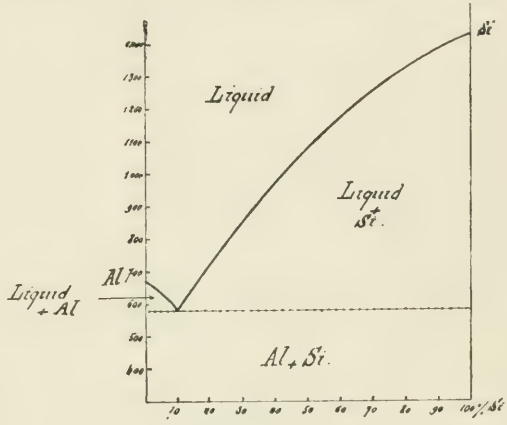


FIG. 418.—Aluminium-silicon diagram (Fraenkel).

solid solutions exist, their maximum solubilities must be extremely low; 0·5 per cent. Si at the one extreme and 2·0 per cent. Al at the other.[1]

Physical and Mechanical Properties of the Metals of Commerce.—These figures will be found tabulated on p. 215.

Effect of Impurities on the Mechanical Properties.—Although but little systematic research has been undertaken in connection with this question [2] it is possible to outline the following general principles:

1. The impurities forming solid solutions affect the crystal grain size: if the grain size increases it is accompanied by an increase in brittleness (phosphorus in iron and steel); if it decreases, there is an increase in strength and elasticity of the material (nickel and chromium in steels).

[1] A research on the combined effects on the mechanical properties of adding different metals to aluminium has been carried out by Schirmeister (*Rev. de Met.*, vol. xii. *cont.*, p. 464, 1915).

[2] See previous footnote.

2. The impurities which separate as individual metals or as separate constituents obey the general laws previously described (see Chap. III., p. 106). But as a general rule there will be a decrease in the percentage elongation.

If the constituent is brittle (example: a compound), the metal will exhibit this property to a greater or less degree and difficulties will be experienced in rolling (bismuth in copper, graphite in nickel).

If the constituent is malleable, there will be a decrease in the percentage elongation but no difficulty in rolling the metal (lead in copper).

Effect of Impurities on the other Physical Properties.—Reference should be made to the remarks on p. 58 in connection with the constitution of alloys.

The importance of the examination of the electric conductivity and the thermo-electric power in determining the existence and limits of solid solutions approaching the compositions of pure metals may again be mentioned.

Uses of the Common Metals of Commerce.—The principal uses of the more common metals will be briefly mentioned before considering the relation between the equilibrium diagrams of the various alloys and their respective uses.

Copper.—Used for a variety of purposes because of its high electrical conductivity, its colour, relative strength at high temperature, and its great ductility and malleability at ordinary temperature. Used in the form of wire (electrical conductors, etc.), plate or sheet which may be easily beaten to shape (locomotive fire-box ends, culinary utensils, etc.), rods (loco. fire-box stays), various tubes.

Tin.—Its principal use is due to its relative chemical inactivity combined with its great ductility. It is used as a coating on other metals (tinned-copper, tin-plate, and in the form of very thin sheet-foil (tin-foil for wrapping foods, etc., for which use it will soon have to compete with aluminium).

Zinc.—Largely used because of its low price and slight oxidation in air; in the form of zinc sheet, tubes, and for galvanising.

Lead.—Owing to its malleability it is mostly used in the form of pipe and sheet; used as a lining to certain vessels including chemical plant owing to its being little attacked by certain reagents, notably sulphuric acid (lining for sulphuric acid chambers, pickling vats, etc.).

Nickel.—Very little used in the form of metal owing to its high cost; its chief uses are dependent on its chemical inactivity with many reagents combined with its relative hardness and toughness. Used for the manufacture of culinary utensils, coinage, and for nickel-plating.

Aluminium.—The use of this metal has been continually increasing since it has been possible to obtain it in the pure state (99·5 per cent.

Metal.	Atomic weight O = 16.	Melting point.	Boiling point.	Density.	Coefficient of expansion × 10^8.	Electric conductivity × 10^4.	Specific heat at 15° C.	Conductivity, heat.	Ultimate strength, tons sq. in.	Per cent. elongation.	Production in tons 1912. World.	Production in tons 1912. France.	Maximum and Minimum price from 1890 to 1912 in francs. Maximum. per 100 kgs.	Maximum and Minimum price from 1890 to 1912 in francs. Minimum. per 100 kgs.	Mean price in francs per 100 kgs.
Aluminium	27·1	658	—	2·60	2313	35·6	0·2089	0·3435	8	30	61,100	13,000	1500 [3]	140·0	220·0
Antimony	120·2	630	1500–1700	6·75	—	2·71	0·0495	0·0442	Metal extr[t] fragile		16,495	4,475	315·60	54·80	55·0
Bismuth	208·0	271	1435	9·80	—	0·92	0·0301	0·0177	Metal extr[t] fragile		—	—	—	—	—
Cadmium	112·4	321	770	8·64	—	14·67	0·0548	0·2213	—	—	—	—	—	—	—
Chromium	52·0	1505	—	6·50	—	?	0·1039	?	—	—	—	—	—	—	—
Cobalt	58·97	1490	—	8·60	—	10·3	0·1030	?	—	—	—	—	—	—	—
Copper	63·57	1083	2100	8·93	1680	64·06	0·0936	0·7198	14	50	1,019,800	12,900	282·80	96·30	184·30
Gold	197·2	1063	—	19·32	—	46·10	0·0316	0·7003	7	30	700[5]	2·7 + 7 Colonies	—	—	344·44[2]
Iron	55·85	1520	—	7·96	1210	13·1	0·1050	0·1665	19	38	1	1	1	1	1
Lead	207·1	327	1450–1600	11·47	2924	5·18	0·0304	0·0836	2	?	1,189,100	33,000	56·80	22·75	45·30
Magnesium	24·32	651	about 1100	1·74	—	23·0	0·2456	0·3760	—	—	—	—	—	—	1500·0
Manganese	54·93	1225	—	7·49	—	?	0·1207	?	—	—	—	—	—	—	450·0
Mercury	202·0	−38·7	357	13·55	—	1·06	0·0335	0·0146	—	—	4,300	Nil	716·0	356·0	657·0
Molybdenum	96·0	2500 (?)	—	8·60	—	?	0·0723	?	—	—	—	—	—	—	—
Nickel	58·68	1452	—	8·00	1279	14·42	0·1084	0·1420 at 97%	31	40	28,500	2,100	590 0	312·0	405·0
Platinum	195·2	1755	—	21·50	—	6·35	0·0316	0·1664	16	10	—	—	750·000	275·000	750·600
Silver	107·88	960	—	10·50	—	68·12	0·0559	1·0960	8	—	7,009	22	19846	7870	10·700
Tin	119·0	232	1700 (?)	7·39	2234	9·61	0·0551	0·1528	5	—	123,100	small	542·90	141·40	391·38
Titanium	48·1	2300 (?)	—	3·54	—	?	0·1125	?	—	—	—	—	—	—	—
Tungsten	184·0	3100 (?)	—	19·10	—	?	0·0336	?	—	—	—	—	—	—	—
Vanadium	51·06	1730	—	5·50	—	?	0·1153	?	—	—	—	—	—	—	—
Zinc	65·37	419	918	7·10	2818	18·6	0·0836	0·2653	3·8	Variable	977,900	61,000	71·70	35·10	65·80

Numerical data (physical and mechanical properties and prices) of the commercial metals:

[1] The figures for iron are too complicated to be included in the table.

[2] Legal value of fine gold 998–1000 in France.

[3] 1890–1892, the price dropped to 625 francs.

[4] Rolled and annealed metal.

[5] For 1911.

Al) (the presence of impurities render it much more readily attacked), and since its cost has been considerably reduced.

The principal uses are :

Aluminium castings of practically pure metal for automobile parts, etc., and in the near future, as cooking utensils to replace those at present manufactured by stamping, pressing, etc., as the metal in the cast condition is not so readily attacked.

Rolled, drawn, stamped metal as sheet, tubes, domestic articles, etc.

As a deoxidising agent (manufacture of steel, copper alloys, etc.).

As a means of obtaining high temperatures and in the preparation or manufacture of certain metals and ferro-alloys (Cr, Mn, W, etc.) by means of the thermit or Goldschmidt reaction.

As an electrical conductor, for which purpose aluminium may, under certain conditions, offer certain advantages as compared with copper.

For the manufacture of thin sheet or aluminium foil which may be used instead of tin-foil.

In the form of powder for the manufacture of metallic paints.

Other metals.—Antimony is only used in the form of alloys.

This also applies to gold and silver.

The metal iron has not been considered in this chapter, but it has been included in the table of physical constants of the pure metals. Iron is very little used in the pure state and as yet electrolytic iron is very difficult to obtain in any quantity.[1]

The effects of various impurities in iron have been already considered (Chap. IV., p. 127, cont.).

COMMERCIAL COPPER ALLOYS

The commercial copper alloys are :

Ordinary brasses (alloys of copper and zinc).

Special brasses.

Ordinary bronzes (copper-tin alloys).

Special bronzes.

Ordinary aluminium bronzes (copper-aluminium alloys).

Special aluminium bronzes.

Cupro-nickels.

Nickel-silvers (copper-nickel-zinc alloys).

1. Ordinary Brasses (Copper-Zinc Alloys)

The only copper-zinc alloys of commercial importance are those in which the copper content exceeds 55 per cent. Cu. Below this content the alloys are too brittle.

[1] In the near future, it will be possible to obtain iron tubes containing less than 0·05 per cent. total impurity ; these tubes are manufactured by electrolytic deposition, and are of interest because of their mechanical properties and extreme thinness.

The diagram will be considered from 40 per cent. Cu (Fig. 419).[1]

Diagram.—*Liquidus.*—The liquidus is always below the melting point of pure copper. It consists of two branches: the curves AB and BC. A solid solution, α, is deposited along AB, and another solid solution, β, along BC.

Solidus.—The solidus consists of two small horizontal sections b_2b_1 and c_1C meeting the transition points B and C, and the two curved sections Ab_2 and b_1c_1.

Below Ab_2 there is the pure α solid solution, and immediately below b_1c_1 the pure β solid solution.

The horizontal Bb_1b_2 corresponds to the reaction

$$\alpha + \text{liquid} \rightleftarrows \beta$$

The horizontal c_1C corresponds to the formation of a third solid solution: γ solid solution.

Transformation Lines.—It will be observed that the diagram given (Fig. 419), which is in accordance with the latest research of Carpenter and Edwards, does not indicate temperatures below 300° C. This is due to the fact that the transformations below a certain temperature are so slow that they no longer need be considered on the diagram.

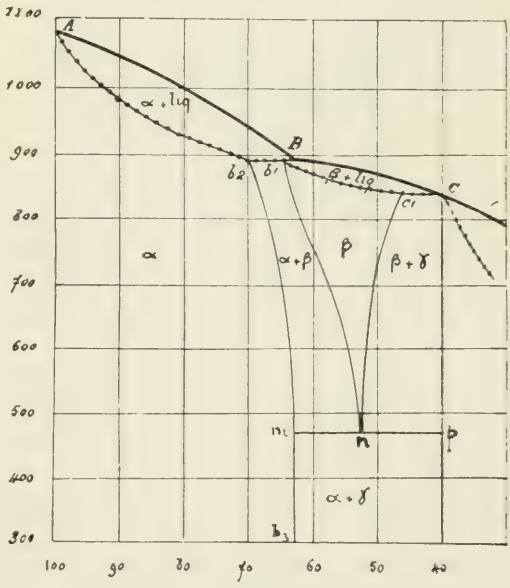


FIG. 419.—Copper-zinc diagram.

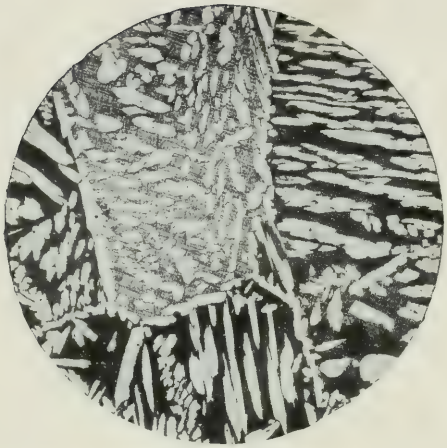
The line limiting the area of the α solid solution, rich in copper, is not vertical, but is a curve of the form b_2mb_3, commencing from the point b_2.

It will be noted that at 300° C., and therefore at atmospheric temperature, the α solid solution may contain between 63 per cent. and 100 per cent. Cu. The diagram shows that the alloys containing between 63–70 per cent. Cu undergo a transformation on heating with the formation of a mixture of $\alpha + \beta$ solid solutions.

The alloys containing between 63 and 40 per cent. Cu will now be examined. They all show two transformation points, the one

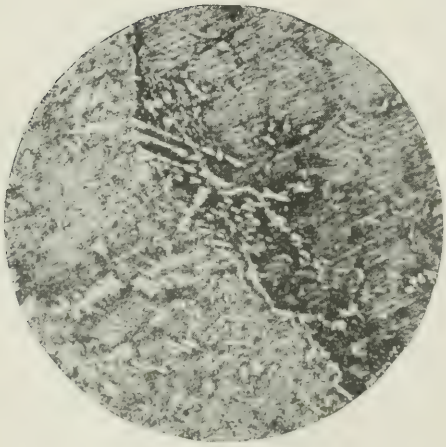
[1] The three series of alloys Cu-Zn, Ag-Zn, and Ag-Cd show a remarkable similarity of diagram and constitution (see Carpenter and Whiteley, *Int. Zeit. Metall.*, vol. iii. p. 145, 1912).

BRASSES (*cont.*).

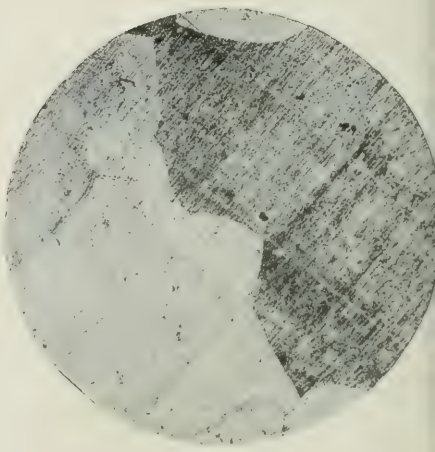


(Cu = 58 ; Zn = 42.)
FIG. 424.—Brass : $\alpha + \beta$.
Etchant : Acid ferric chloride.
(× 50)

(Cu = 56·5 ; Zn = 43·5.)
FIG. 425.—Brass : $\alpha + \beta$.
Etchant : Ammoniacal copper solution.
(× 50.)



(Cu = 55·7 ; Zn = 44·3.)
FIG. 426. β brass with a little α.
Etchant : Acid ferric chloride.
(× 50.)



(Cu = 53.)
FIG. 427.—Pure β brass.
Etchant : Acid ferric chloride.
(× 50.)

For other alloys :

Water	100 c.c.
Hydrochloric acid	6 c.c.
Ferric chloride	19 gms.

These solutions darken (blacken) the β constituent, the α solid solution remaining unaffected.

Pure α solid solution has the appearance of a heterogeneous solid solution in cast brass ; the dendritic formation is easily visible at low magnifications ; when rolled and annealed, the usual structure consists of a number of irregular grains of varying colour exhibiting marked twinning (see Pl. XXV to XXXII., p. 120).

When the structure consists of α+apparent β, the β_1 constituent is always more coloured than the α constituent in contact with it (Figs. 421–423, Pl. LXXVI.) ; but this β_1 coloration in cast brass varies with different grains, according to the order of solidification of the primary crystals (Fig. 424, Pl. LXXVII., and Fig. 433, Pl. LXXIX., p. 227), in such a manner that it is possible to find the α of one grain more coloured than the β_1 of another grain. In any given grain, the β_1 is always more readily coloured or etched than the α solid solution. This slight complication is greatly lessened in alloys that have been subjected to mechanical treatment.

Finally, it will be observed from the micrographs that, between 53 per cent. and 63 per cent. Cu there is a direct relation between the copper content and the constitution of the alloys.

Various Physical Properties.—The examination of the electrical resistance of these alloys has shown a sharp variation to occur beyond the range with which we are at present concerned. The examination of the electro-chemical potential of these alloys, in recent researches by Pouschine, has shown sharp variations to occur corresponding to the definite compounds Zn_6Cu, Zn_2Cu, ZnCu and $ZnCu_2$, which probably exist in solid solution.

Relation between the Diagram and the Mechanical Properties at Ordinary Temperatures.—One of the authors has recently renewed the investigation into the relation between the constitution and the mechanical properties of the copper-zinc alloys. It may be observed that the classical curves, produced by Charpy, giving the elongation and the ultimate strength, found by tensile tests, show certain inexplicable irregularities ; a maximum elongation for 70 per cent. Cu, a maximum ultimate strength with 57 per cent. Cu. But it is known that with compositions corresponding to the $\alpha+\beta$ structures, the mechanical properties should vary directly along a straight line, at least as far as the eutectoid point.

The curves, Fig. 419, give the results obtained by one of the authors with rolled and annealed alloys. The curves for the elongation

and ultimate strength are practically of the same form as those given by Charpy ; the difference in the actual results can undoubtedly be explained by the method of preparation of the alloys (cold or hot rolling according to composition). But the additional figures

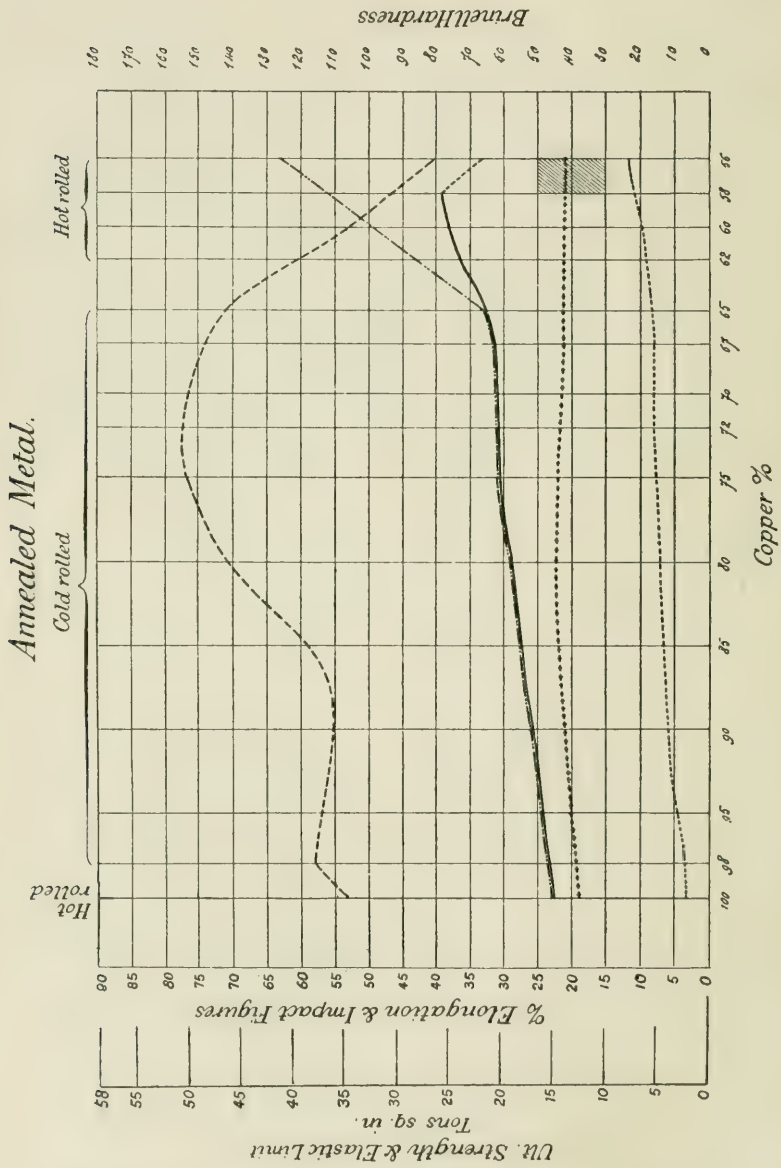


FIG. 428.—Properties of the copper-zinc alloys

for hardness and impact tests give confirmation to the law of proportionality.

If this is not evident from the ultimate strength of the alloys, it is owing to the relative brittleness of the alloys introducing errors

into the test. As regards the elongation figures, the maximum exactly coincides with the appearance of the transformation point and the possibility of the existence of a little β_1 on cooling.

For further details reference should be made to the original paper.[1]

Relation between the Diagram and Treatment.—The mechanical treatment, which is of considerable importance, proceeds directly according to the diagram.

Copper may be forged either hot or cold. The α solid solution, at least when of relatively low zinc content, should exhibit similar properties. Thus it is possible tc roll copper-zinc alloys containing above 90 per cent. Cu either hot or cold, provided they are very free from impurities. The α solid solution containing between 63–90 per cent. Cu cannot be cold-rolled. Thus, if the curves showing the variations of mechanical properties with change of temperature are examined (Figs. 142, 143, p. 112) it will be seen that the elongation of a brass containing 70 per cent. Cu decreases rapidly with rise of temperature and only increases again through a small temperature range (between 650°–750°). The elasticity (impact figure) remains very low above 300°. The β solid solution is malleable whilst hot but not cold. Thus the brasses containing between 53–63 per cent. Cu are malleable whilst hot (650°–800° C.). They are only malleable cold when they contain very little of the β constituent, and this quality is therefore confined to alloys containing 60–63 per cent. Cu.

These results may be summarised as follows :—

1. Brasses consisting of α solid solution may always be cold worked.

2. α brasses can only be worked hot when of high copper content (90–100 per cent. Cu).

3. Brasses consisting of α and β can only be worked at high temperature (between 650°–800°), except when they contain only small amounts of β (Cu=60–63 per cent.) when they may also be cold-worked.

With alloys consisting of a single constituent, mechanical treatment followed by annealing produces a very regular and clearly outlined polygonal structure (see Figs. 196–199, Pl. XXXI., p. 121).

The various mechanical treatments which are carried out at ordinary temperature such as drawing, stamping, etc., may be more easily performed the greater the elongation and the lower the elastic limit of the material. Therefore it is the alloys consisting of the α solid solution which yield the best results with this type of treatment and more especially those containing approximately 70 per cent. Cu. However, all these alloys may be drawn down into wire, but the alloys containing two constituents require more power

[1] Guillet, *Rev. de Met.*, vol. xi. p. 1094, 1914.

and greater precautions to be taken in this operation (such alloys require to be more frequently annealed).

Heat treatment other than annealing is not of great importance with these alloys: the structure of the alloys containing between 63 and 55 per cent. Cu practically corresponds to the structure of a quenched alloy. Alloys containing between 63 and 70 per cent. Cu may be quenched with beneficial results, but a similar structure may be more economically obtained by the addition of zinc to the alloy.

The annealing of cold-worked brass produces effects which have already been considered. These effects have been studied more especially by Charpy and Grard, and their results have already been quoted in considering the general conditions of annealing (Chap. III., p. 121).

Relation between the Diagram and the Industrial Uses.—A primary factor in the choice of an alloy of any definite composition is the question of cost, and this is essentially dependent on the zinc content. Again, the colour is frequently of great importance; alloys very rich in copper (90 per cent. Cu) of reddish colour or the so-called gilding alloys (80–85 per cent. Cu) are used for cheap jewellery. Brass plate and sheet is nearly always of pure α composition. To avoid manufacturing difficulties, alloys required for spinning or stamping, as in the manufacture of brass cartridge cases, should contain approximately 70 per cent. Cu; the composition of French cartridge case brass is 67 per cent. Cu, 33 per cent. Zn.

In all cases, in spite of the increased cost, it is better to choose an alloy of composition to the left of the maximum elongation point rather than to the right of this composition to obtain a given elongation; this is due to the fact that alloys containing above 70 per cent. Cu show no transformation point and therefore contain no β constituent, no matter what annealing treatment they may have received.

For the manufacture of very thin sheet or foil (Dutch metal) alloys of similar structure are used.

For manufacturing processes and uses that do not require such high elongation, alloys of lower copper content, and therefore of less cost, may be used; the alloys containing 65 per cent. Cu (brass sheet) and 62 per cent. Cu are frequently used, but the alloy with 62 per cent. Cu contains a little β constituent.

Muntz metal (60 per cent. Cu) can be worked hot and the rolled alloy was used as sheathing metal for ships. This alloy with 1–2 per cent. lead added gives a brass of reduced strength and ductility but possessing greatly improved machining qualities.

In some instances the copper content of brasses will be found as low as 56·5–57·5 per cent. Cu.

Brass wire and rod may be of varying composition. Ordinary free-machining or free-cutting brass contains 58–61 per cent. Cu,

0·5—1·0 per cent. impurities, and not more than 1–2 per cent. lead, the effect of which will be described later. Such an alloy gives approximately the following figures on test: Ult. strength=20 tons sq. in.; percentage elongation=30. Brasses of relatively low copper content are used both because of their lower cost and because they machine more easily than those of higher copper content.

For certain purposes, stampings, etc., where the elongation is of importance, those of high copper content must be used: 62, 65, 67, 70, and even 72 per cent. copper is quite usual. Brasses containing 82, 88, 90 per cent. Cu are only used in certain special instances (jewellery).

The alloys used for the manufacture of brass tube usually contain 62–70 per cent. Cu.

The alloys for hot forging, pressing, drawing, and stamping contain between 55 and 62 per cent. Cu, and consist of two constituents.

Castings are of very variable composition; they are frequently cast from old metal remelted. However, it should be noted that the brasses of α composition (usually 62–67 per cent. Cu) have a much lower coefficient of contraction than the $\alpha+\beta$ brasses (58–62 per cent. Cu), but the latter are much stronger. The addition of lead imparts easy machining qualities.

Then, there is the use of brass as brazing solder, in which case the melting point, shown by the diagram, is of great importance; brazing solder for iron, which may have a high melting point, contains between 67–72 per cent. Cu, whilst that for brass and copper contains between 48 per cent. and 55 per cent. Cu and is of lower melting point.

Special Brasses.

Special brass is the term applied to a copper-zinc alloy to which a third element has been intentionally added.

The theory of the special brasses is applicable to the three principal groups of commercial copper alloys: copper-zinc, copper-tin, and copper-aluminium, and a short summary of the work of one of the authors on this subject will be given.[1]

If a third element is added to a copper-zinc alloy three conditions may arise.

1. The element added separates in the free condition: this is the case with lead (Pl. LXXVIII., Figs. 429, 430, see p. 226).

2. The element added forms a separate constituent; this occurs with phosphorus and tin.

3. The element enters into solution in the constituent or constituents of the copper-zinc alloy. This is the most usual case.

[1] Guillet, *Rev. de Met.*, vol. iii. p. 143, 1906.

It is possible, moreover, that in the first case the elements at first enter into solid solution, but that the solid solution can only retain a very small percentage of the element added.

As previously stated, on the appearance of a new constituent in an alloy, the mechanical properties of such an alloy decrease in value.

Thus the addition of lead to a brass lowers the ultimate strength and elongation, but brasses of this composition are sometimes of industrial importance. Two typical examples may be quoted.

All free-cutting or machining brass, if it is to work satisfactorily in automatic machines and give good turnings, should contain 1 to 3 per cent. lead; the lead separating throughout the mass in the form of minute globules, forms planes of weakness along which the metal is broken away (sheared) by the tool.

Brass to resist the action of sea-water, and probably fresh-water, contains 1 per cent. tin and usually 60–62 per cent. Cu (naval brass). There is then formed, instead of the partially transformed β solution, a constituent which appears to resemble the δ solution of the bronze series.

It has already been stated that the most general case is that in which the added element enters into solid solution with one or both of the constituents of the copper-zinc alloy.

A typical example may be considered:

Consider an alloy:

$$Cu=70 \quad Zn=30$$

and compare it with an alloy of the same copper content, but in which 4 per cent. of the zinc content has been replaced by another element M; the composition will then be:

$$Cu=70 \quad Zn=26 \quad M=4$$

Microscopical examination of the two alloys will show the first alloy to consist of a pure α solid solution, whilst the second alloy will show an $\alpha+\beta$ structure, the two constituents being present in the same proportions as found in an ordinary brass of composition:

$$Cu=58{\cdot}5 \quad Zn=41{\cdot}5$$

Thus, such a special brass is stated to have:

An actual composition (found by chemical analysis): Cu=70.

An apparent composition (found by microscopical examination): Cu=57.

The approximate apparent content can only be found, by microscopical examination, within the limited range of composition existing between 53 and 63 per cent. Cu, in which range two constituents are present. From the microscopical examination it follows that the addition of 4 per cent. of the element M is equivalent to adding a certain quantity of zinc.

If the term, equivalent coefficient of the element M, is applied to the amount of zinc which is substituted by 1 per cent. of this special element, the composition of the alloy being referred to 100, then the relation which exists between the real and apparent compositions may be found.

Example: If the equivalent coefficient (t) of the special element $M=t=6$.

The preceding alloy of composition: Cu=70, Zn=26, M=4 will have an apparent composition:

$$Zn=26+4\times 6=50$$

which reduced to a percentage (100) is:

$$Zn=\frac{50\times 100}{70+50}=41{\cdot}6$$

Therefore the apparent copper content is Cu=58·4.

Let A be the real percentage content of copper; B the real percentage content of zinc; q the percentage amount of the additional element added, and t the equivalent coefficient of this element; A′ the apparent content of copper; B′ the apparent content of zinc. Then:

$$A+B+q=100$$
$$A'+B'=100$$

But $B'=B+tq$ reduced to 100 basis; then

$$B'=\frac{(B+tq)100}{A+B+tq}$$

Therefore $$A'+\frac{100(B+tq)}{A+B+tq}=100$$

then: $$A'(A+B+tq)=100A$$

But $A+B=100-q$: $$A'(100-q+tq)=100A$$
$$A'q(t-1)=100(A-A')$$

Therefore $$(1)\quad q=\frac{100(A-A')}{A'(t-1)}$$

where q=the percentage amount of special element of equivalent coefficient, t, required to obtain an alloy of real copper content A, and apparent content A′.

$$(2)\quad A'=\frac{100A}{100+q(t-1)}$$

this equation gives the apparent copper content A′ of an alloy of actual content A, to which has been added a quantity q, of a special element of equivalent coefficient t.

$$(3)\quad t=1+100\frac{A-A'}{qA'}$$

this equation shows the equivalent coefficient t of the special element which added in quantity, q, to an alloy of actual content A, gives it an apparent content A′.

These formulæ show that if t is greater than unity, the apparent content (Cu) is less than the real content; whilst if t is less than unity the apparent content is greater than the real content.

Tests carried out by one of the authors with this object have enabled the following approximate equivalent coefficients to be determined.

Si=10, Al=6, Mn=0·5, Fe=0·9, Ni=−1·3.

Silicon and aluminium give an apparent content appreciably lower than the real content (Pl. LXXVIII., Figs. 431, 432), iron causes practically no alteration, manganese and more particularly nickel give an apparent content that is greater than the actual content of copper (Pl. LXXIX., Figs. 433–436).

The practical use and interest of the apparent content requires consideration.

A comparison of an ordinary brass of definite composition with a special brass of the same *apparent* composition will show the two to possess similar properties, but the special brass will be stronger and superior to the former alloy.

Two typical examples may be quoted:

(1) *Manganese brass* (Cu=55, Zn=40, Mn=5).—Apparent composition by examination, 56·5; by calculation (Mn coef.=0·5)=56·4.

The rolled and annealed metal gave the following tests: ult. strength=31·5 tons. Elastic limit=15·8. Percentage elongation=25.

The alloy of actual composition Cu=56·5, Zn=43·5 under similar conditions gave: ult. strength=28·4 tons. E=8·8 tons. Percentage elongation=18.

(2) *Nickel brass* (Cu=55·2, Zn=42·3, Ni=2·5).—Apparent composition by examination=58·0 per cent. Cu; by calculation (Ni coef.=−1·3)=58·4 per cent. Cu.

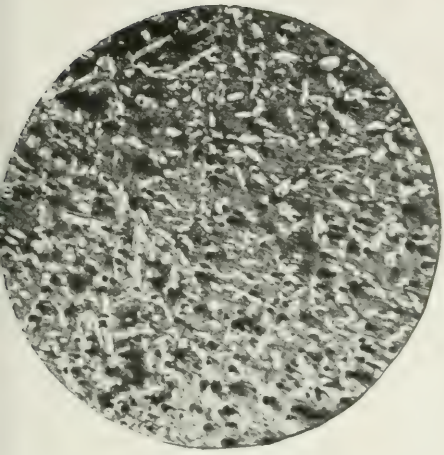
The rolled and annealed metal gave the following tests: ult. strength=28·7 tons. E=8·25 tons. Percentage elongation=33.

The reduction in area could not be measured, owing to the deformation and irregularities of the surface.

The alloy of actual composition Cu=58, Zn=42, under similar conditions gave tests as follows: ult. strength=25·2 tons. E=7·6 tons. Percentage elongation=25.

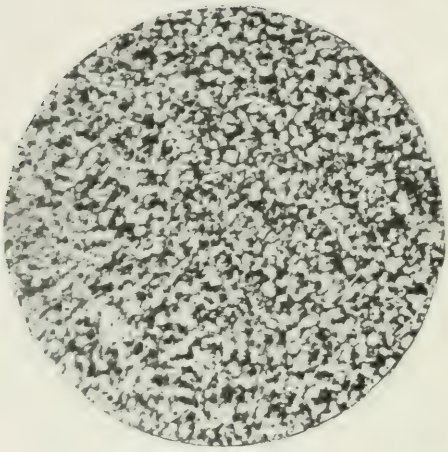
It will be observed that microscopical examination alone enables the apparent composition to be determined, when such content is between 54 and 63 per cent. Cu, and also determines whether the metal may be worked hot or cold, as this is only dependent on the apparent composition (constitution).

SPECIAL BRASSES.



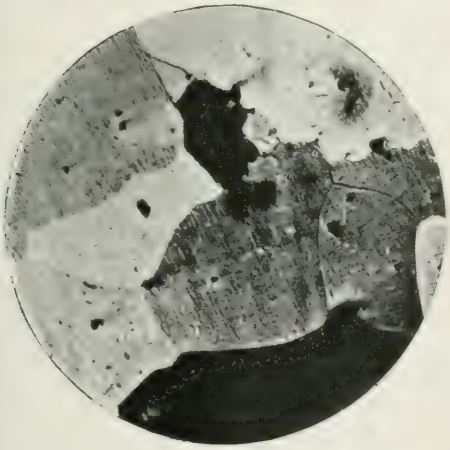
(Cu = 55; Zn = 40; Pb = 5.)

FIG. 429.—Lead brass.
Rolled, drawn and annealed.
(× 50.)



(Cu = 59; Zn = 40; Pb = 1.)

FIG. 430.—Lead brass.
Free cutting brass, rolled, drawn and annealed.
(× 50.)



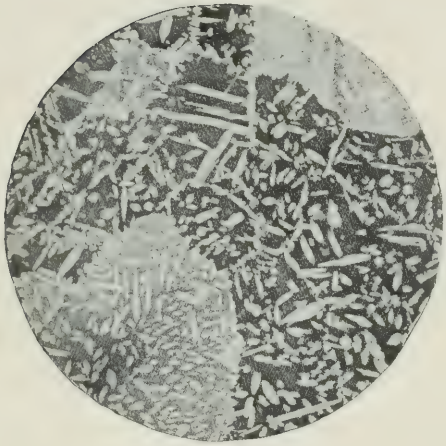
(Cu = 60; Zn = 36; Al = 4.)

FIG. 431.—Aluminium brass.
β constituent.
Etchant: Ammoniacal copper solution.
(× 50.)

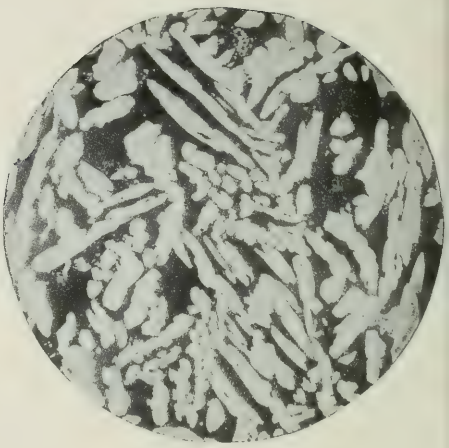
(Cu = 67; Zn = 29·5; Al = 3·5.)

FIG. 432.—Aluminium brass; $\alpha + \beta$.
The same constitution as Cu = 57; Zn = 43.
Etchant: Ammoniacal copper solution.
(× 50.)

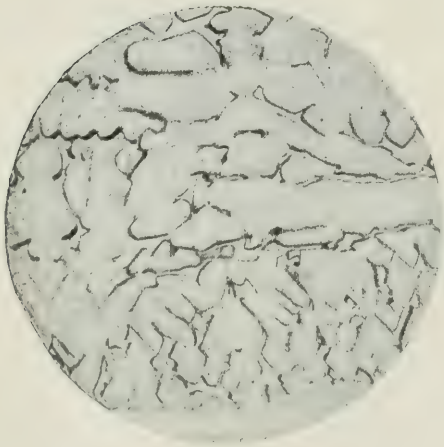
SPECIAL BRASSES (*cont.*).



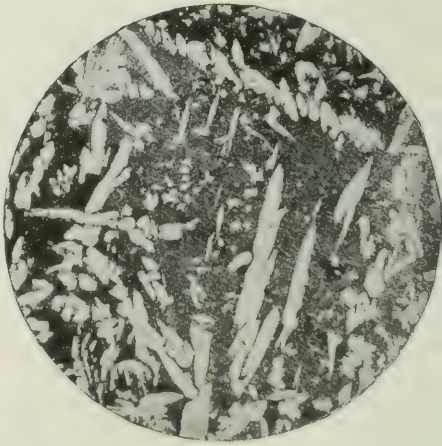
(Cu = 55 ; Ni = 0·5.)
FIG. 433.—Nickel brass.
Etchant : Acid ferric chloride.
(× 30.)



(Cu = 56 ; Ni = 2.)
FIG. 434.—Nickel brass.
Sand cast : Annealed at 750° C.
Etchant : Acid ferric chloride.
(× 57.)



(Cu = 55·4 ; Ni = 5·0.)
FIG. 435.—Nickel brass.
Sand cast : As cast.
Etchant : Acid ferric chloride.
(× 200.)



(Cu = 49·4 ; Ni = 5·2.)
FIG. 436.—Nickel brass.
Sand cast : Annealed at 750° C.
Etchant : Acid ferric chloride.
(× 57.)

It must be noted that actually the equivalent coefficient has a definite value for the lower limit of the α solution (minimum content of copper in this solution), and a different value for the upper limit of the β solution (maximum content of copper in this solution).

These two values enable the apparent composition to be calculated for any alloy according to its composition, the value of the equivalent coefficient varying directly between the two extreme limits. When the range of composition corresponding to the existence of two constituents is limited, as in the case of the brasses and also the aluminium bronzes—but not in the case of the bronzes (copper-tin series)—it is possible in practice to employ one value for the equivalent coefficient.

The principal special brasses are :

Those containing lead, which are termed free-cutting or free-machining brasses.

Those containing tin—naval brasses used in ship construction and for articles subject to sea-water corrosion.

Those containing aluminium, manganese, or iron, and usually more than one of these elements, known under the general term *high tensile bronzes.*

Those containing nickel, which have only recently been studied and appear to be of considerable interest, because of the increase in malleability due to the presence of this element.

But generally, and unjustifiably in the authors' opinion, extremely complex alloys are frequently employed in commercial practice.

A typical example is :

Cu=51·74	Pb=0·89	Sn=0·31	Fe=1·43
Zn=37·03	Mn=1·99	Al=2·34	Ni=3·34

There can be no doubt that an equally good result could have been obtained with a far less complex composition and at the same time a simpler and less costly melt.

In practice it is possible to obtain special brasses that will give figures within the following limits in the rolled and annealed condition:

Ult. st. $= 35$ tons $E \leqq 20$ Percentage elongation $\geqq 40$

3. **Ordinary Bronzes (Copper-tin Alloys)**

The simple copper-tin alloys or ordinary bronzes are used commercially when they contain over 75 per cent. Cu. For theoretical reasons, and in order to include the speculum metals, formerly used for mirrors, and containing up to 40 per cent. Sn, the alloys containing between 100 per cent. and 50 per cent. Cu will be considered.

The copper-tin diagram is due, principally, to the researches of Heycock and Neville, Shepherd and Upton, and Giolitti and Tavanti.

The authors have modified it at certain points,[1] in order that it may conform with the general principles of the constitution of alloys (Fig. 437).

Diagram.—*Liquidus.*—The liquidus consists of three curved sections: AB, commencing from the melting point of pure copper and steeply inclined to the horizontal; BC, very short; and CD, very much less inclined.

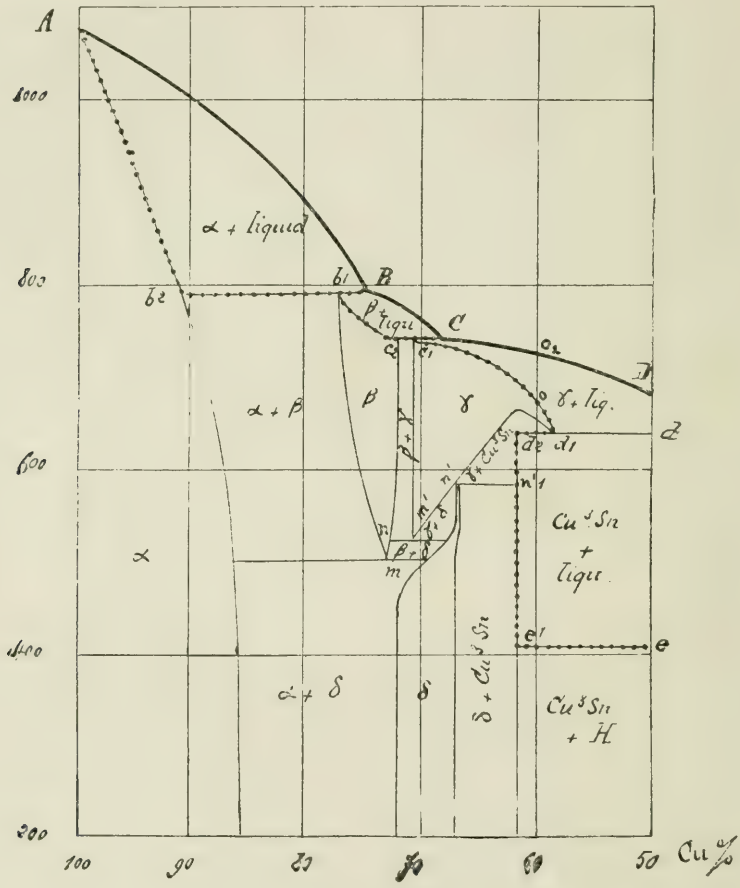


FIG. 437.—Copper-tin diagram.

An α solid solution separates along AB; along BC a β solid solution; and along CD a third solid solution, γ solution.

Solidus.—The solidus consists of three inclined branches Ab_2, b_1c_2, and c_1d_1, showing the completion of solidification of the three solid solutions α, β, γ, and three horizontals b_2b_1, c_2c_1, and d_2d_1, corresponding to the three transition points B, C, and D. With this last point, owing to the disposition of the curves in the vicinity of

[1] Refer Portevin, *Rev. de Met.*, vol. vi. *a*, p. 479, 1909; also Slavinsky, *Rev. de Met.*, vol. xii. *a*, 405, 1915.

the horizontal d_2d_1d, it will be observed that on passing the horizontal with decreasing temperature, there will be an increase in the quantity of liquid present owing to the reaction.

$$\gamma \text{ (of composition } d_1) \rightarrow Cu_3Sn(\text{point } d_2) + \text{liquid D}$$

Similarly with the alloys between d_1d_2, which are completely solidified above the horizontal, there is the appearance of liquid; thus a partial fusion during cooling occurs.

If an alloy containing 60 per cent. Cu be considered: It is solid below the horizontal e_1e, partially liquid between e_1e and d_2d; again becomes entirely solid between this line (d_2d) and the point O, passes into the partially liquid condition between O and O_1, becoming entirely liquid above O_1.

Transformation Lines.—The copper-tin alloys present one of the most complex examples of transformation lines. As with the brasses, it will be observed that the temperature scale does not extend to atmospheric temperature, but stops at 200° C.

The α solid solution area is outlined on the right by a curve, showing a minimum of 87 per cent. Cu between 200° and ordinary temperature.

Thus the bronzes containing less than 13 per cent. Sn consist of only one constituent. In actual practice, in cast alloys, the δ constituent is also present, and will be described later (alloys containing 8 per cent. Sn). Prolonged annealing enables equilibrium conditions to be attained with the consequent disappearance of this constituent as previously explained (Chap. II., p. 82).

The pure β solid solution solidifies along b_1c_2; but the limits of this solid solution vary with the temperature. Consequently this solid solution, on cooling, liberates α along the line b_1m, the γ solution along the curve c_2n, and finally a third solid solution, δ, along the small section nm. The solid solution β gives place to a eutectoid of $\alpha + \delta$ along the horizontal at m. Therefore, below the horizontal tm there are the solid solutions α or δ and their eutectoid. Moreover, owing to the shape of the curves outlining the $\alpha + \delta$ area, there is, subsequent to the formation of the $\alpha + \delta$ eutectoid, a deposition of δ surrounding the eutectoid areas (Fig. 442, Pl. LXXXI., p. 232).

The γ solid solution solidifies along c_1d_1 and the limits of composition vary with the temperature, as in the case of the β solution. The solution changes in composition liberating the β solid solution along $c'm'$, the compound Cu_3Sn along the curve d_1n' and the δ solid solution along the curve $n'm'$. The point m' corresponds to the eutectoid $\beta+\delta$ and between the horizontal at the point m' and that at the point m, β or δ exist together with their eutectoid.

Finally, along the horizontal $n'm'$, the following reaction occurs:

$$\gamma + Cu_3Sn \rightleftarrows \delta$$

This complex section of the diagram has been variously considered by different authorities; there is no necessity to consider this question more deeply in the present instance, since the compositions of the commercial bronzes used for engineering and similar work do not lie within this area.

Constituents (Pls. LXXX.–LXXXVI., p. 232).—The constitution at 200° C. is taken, since it is identical at atmospheric temperature.

Between 100 and 87 per cent. Cu: α solid solution.

Between 87 and 72 per cent. Cu: α solution, δ solution and their eutectoid.

Between 72 and 67 per cent. Cu: δ solution.

Between 67 and 61·6 per cent. Cu: δ solution $+Cu_3Sn$.

Between 61·6 and 50 per cent. Cu: Cu_3Sn + solid solution closely approaching CuSn.

The usual etchants are as follows:

Ferric chloride serves as a means of identifying the constituent δ, which appears of a bluish-white colour after etching.

Sodium picrate darkens the δ constituent.

Ammoniacal copper solution.

Sodium hydrate or ammonia + hydrogen peroxide, which, *acting as an oxidising agent*, clearly reveals the chemical heterogeneity of the unannealed α solid solution.

For quenched bronzes the same etchants may be used: β is blackened by ferric chloride, whilst δ retains its bluish colour.

In cast bronzes consisting of the pure α solution, the chemical heterogeneity of this solution may be clearly shown by oxidising etching (Fig. 107, Pl. XIII. *cont.*); at low magnifications the dendritic structure is clearly seen. The dendritic structure is even more evident in alloys containing the eutectoid when the α dendrites appear of varying colour from pale yellow to dark fawn and are very clearly outlined by the surrounding eutectoid, to which δ gives its characteristic bluish-white colour (Fig. 445, Pl. LXXXI.; Figs. 446, 447, Pl. LXXXII.). At higher magnifications, the eutectoid is resolved into $\alpha+\delta$ (Fig. 442, Pl. LXXXI.; Fig. 449, Pl. LXXXII.), the α being of varying shades of yellow and the δ bluish white; the δ, which is easily visible after simple polishing owing to its bluish-white appearance, forms a border round the eutectoid (Fig. 442, Pl. XXXI. and Fig. 449, Pl. LXXXII.). The formation of this border is due to the deposition of δ subsequent to the formation of the eutectoid as shown by the lines of the diagram. The α solid solution often presents a striated appearance, and this structure may be traced to the effects of cold-work. The β constituent appears either homogeneous (Fig. 452–454, Pl. LXXXIII.) or needle-shaped (Fig. 453, Pl. LXXXIII.), and is sometimes surrounded, when mixed with α, by a fine border of δ (Fig. 443, Pl. LXXXI.).

Various Physical Properties.—The determination of the expansion, electro-chemical potential, thermal and electric conductivities, thermo-electric power, density and heat of formation as functions of the composition have indicated the presence of the compound Cu_3Sn, the existence of which no longer remains in doubt.

Relations between the Diagram and the Mechanical Properties at Atmospheric Temperature.—The curves shown in Fig. 465 give the ultimate strength, elastic limit, and percentage elongation for alloys of tin content between 0 per cent. and 20 per cent. Sn. It will be observed that between 0 per cent. and 18 per cent. Sn the tests have been made on rolled and annealed material and between 10 and 20 per cent. Sn on cast material.

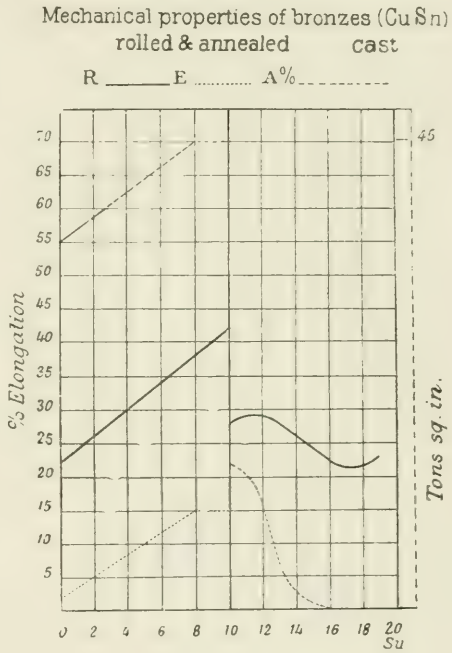


FIG. 465.

Further, with rolled material, the ultimate strength increases regularly with the tin content; the same applies to the elastic limit and percentage elongation up to 8 per cent. Sn; they then appear to remain constant between 8 and 10 per cent. Sn. With cast material it was found impossible to determine the elastic limit with any accuracy; the elongation is zero above 18 per cent. Sn and at this point, the alloys becoming so brittle, the ultimate strengths are open to question.

Moreover, in accordance with the law of proportionality the properties of the $\alpha+\delta$ alloys should vary along a straight line. If this is not the case, it will be due to their brittleness and their heterogeneity in the cast state.

There is thus a direct relation between the properties and the constitution: the α solution is malleable, whereas the hard and brittle δ solution, although giving certain frictional qualities to the material, decreases the elongation and elasticity (impact).

It should be stated that the δ constituent of industrial bronzes is present in the form of eutectoid, as shown by the point *m* on the diagram.

Thus the mechanical properties of the α solid solution bronzes are of interest as regards malleability combined with strength.

The bronzes of $\alpha+\delta$ constitution are hard and brittle in proportion to their δ content, and therefore, with similar conditions of cooling, to their content in tin.

Relation between the Diagram and Treatment.—*Mechanical treatment.*—The α solid solution is malleable when cold but not when hot, except when the composition approximates to pure copper. The δ solid solution is brittle; it destroys the malleability of the alloy, even when present in the eutectoid condition. The β solid solution is considerably more malleable. It may therefore be assumed that the only bronzes suitable for cold-working are those containing less than 13 per cent. Sn, and that, owing to their heterogeneity, the bronzes containing over 10 per cent. Sn can only be rolled with difficulty. The $\alpha+\delta$ bronzes cannot be cold-worked. If great precautions are taken they may be worked hot (gongs).

Heat Treatment.—*Quenching.*—The $\alpha+\delta$ bronzes are affected by quenching (only those alloys used for mechanical purposes will be considered). The diagram indicates the transformations that are brought about by this form of treatment, the quenching temperature being above 500° C. The quenching effect is only partial for those alloys that have an $\alpha+\beta$ constitution at high temperature.

The β constituent is obtained by quenching, and appears either homogeneous (Fig. 443, Pl. LXXXI.) or with an acicular or needle-shaped appearance (Fig. 453, Pl. LXXXIII.), somewhat similar to martensite in steels. On tempering, the α constituent separates from the β solution in the form of oriented needles.[1]

The modifications of the mechanical properties produced by quenching are usually as follows: there is an increase in the ultimate strength and frequently in the malleability of the alloy, but in some instances the increase in malleability may be attributed to the decrease in brittleness, permitting a more even fracture of the tensile test-piece. Several typical results obtained by one of the authors[2] during some research on quenched bronzes are given in the following table (the figures were obtained from a bronze containing 20 per cent. Sn):

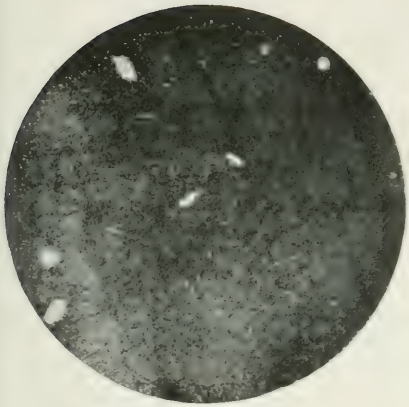
Condition.	Ult. strength (tons sq. in.).	E (tons sq. in.).	Percentage elongation.
Unquenched	15·21	8·64	3
Quenched from 500° ..	13·69	?	3
,, ,, 600° ..	17·67	5·30	10
,, ,, 700° ..	17·67	6·56	13
,, ,, 750° ..	19·25	?	19
,, ,, 800° ..	16·03	5·30	9

[1] A similar effect is observed by annealing quenched brasses (ref. Portevin, *C. R.*, 158, 1174, 1914).

[2] Guillet, "Etude industrielle des alliages metalliques," vol. ii. p. 494, Dunod and Pinat.

BRONZES.

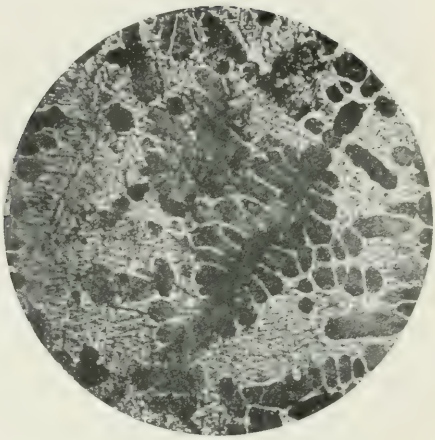
(Heycock & Neville.)



(Cu = 92·8 : Sn = 7·2.)

Fig. 438.—Chilled from 800° C. Homogeneous α solution.

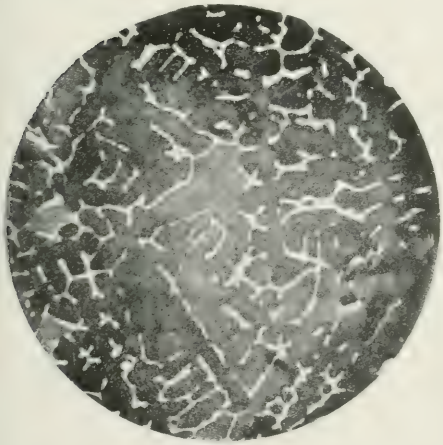
Etchant : Bromine in hydrochloric acid.
(× 45.)



(Cu = 96·3 ; Sn = 3·7.)

Fig. 439.—Chilled from 1025° C. Primary α crystals, dark.

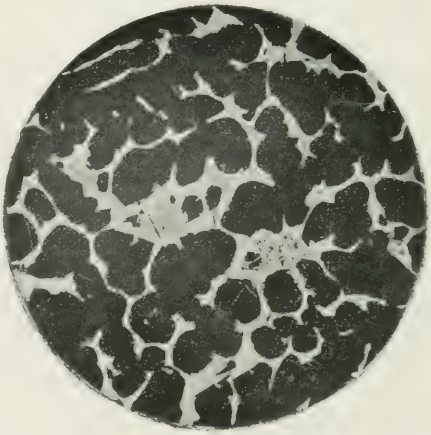
Etchant : Acid ferric chloride.
(× 45.)



(Cu = 96·3 ; Sn = 3·7.)

Fig. 440.—Copper tin alloy. Chilled from 957° C. (α + liquid).

Etchant : Acid ferric chloride.
(× 10.)

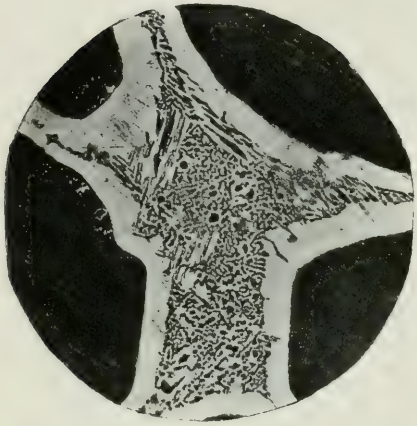


(Cu = 84·4 ; Sn = 15·6.)

Fig. 441.—Copper tin alloy. Chilled from 470° C. α dark ; eutectoid, light.

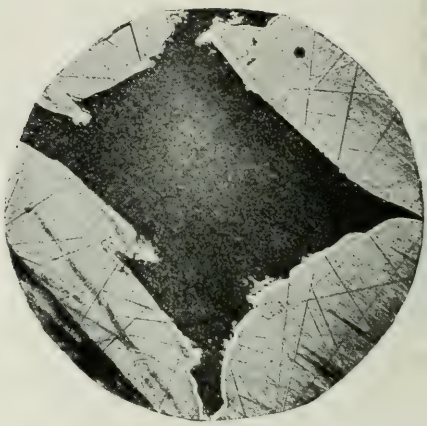
Etchant : Acid ferric chloride.
(× 18.)

BRONZES (*cont.*).



(Cu = 84·4 ; Sn = 15·6.)

FIG. 442.—Copper tin alloy.
Chilled from 470° C.
Dark primary α crystals surrounded by a border of white δ in a ground mass of black eutectoid ($\alpha + \delta$).
(× 280.)
(HEYCOCK & NEVILLE.)



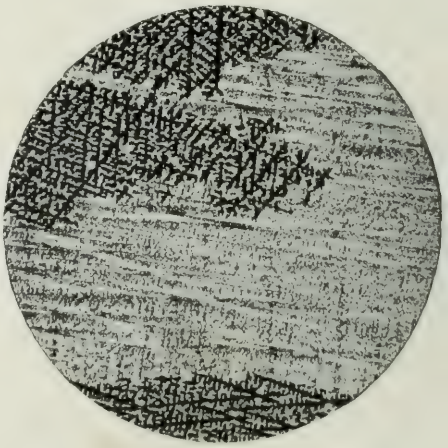
(Cu = 84·4 ; Sn = 15·6.)

FIG. 443.—Copper tin alloy.
Chilled from 546° C.
Dark secondary β separated from the half-tone areas of α by a white border of δ.
(× 280.)
(HEYCOCK & NEVILLE.)

Etchant : Acid ferric chloride.

(Cu = 84·4 ; Sn = 15·6.)

FIG. 444.—Chilled from 880° C.
α surrounded by rapidly chilled liquid.
Etchant : Acid ferric chloride.
(× 120.)
(HEYCOCK & NEVILLE.)



(Cu = 83·6 ; Sn = 16·4.)

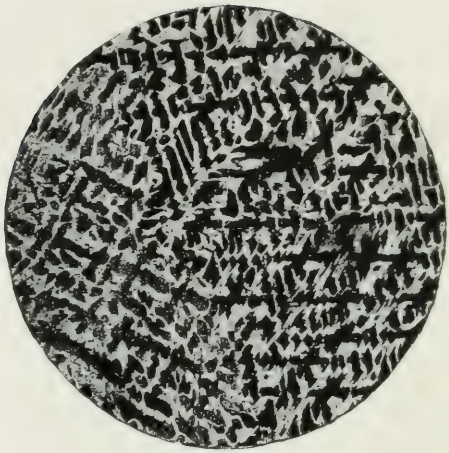
FIG. 445.—Ordinary bronze.
Chill cast : As cast.
Dendrites of α.
Etchant : Acid ferric chloride.
(× 57.)

BRONZES (*cont.*).

(Cu = 79·7 ; Sn = 20·3.)

FIG. 446.—Ordinary bronze.
Chill cast : As cast.
Dendrites of α outlining several crystals

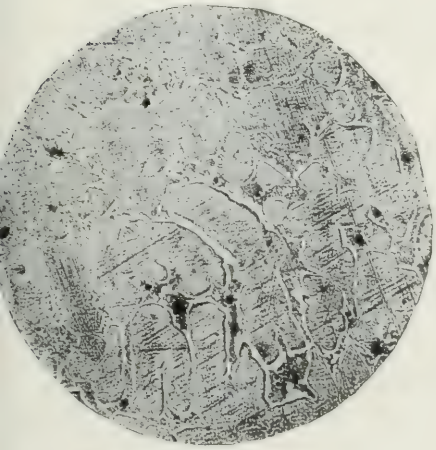
Etchant : Acid ferric chloride.
(× 57.)



(Cu = 79·7 ; Sn = 20·3.)

FIG. 447.—Ordinary bronze.
Dark dendrites of α ; light eutectoid.

Etchant : Acid ferric chloride.
(× 57.)



(Cu = 79·7 ; Sn = 20·3.)

FIG. 448.—Ordinary bronze.
Sand cast : As cast.
α and eutecteid δ.

Etchant : Acid ferric chloride.
(× 200.)

(Cu = 79·7 ; Sn = 20·3.)

FIG. 449.—Ordinary bronze.
Sand cast : As cast.
α and eutectoid δ.

Etchant : Acid ferric chloride.
(× 530.)

BRONZES (*cont.*).

(Heycock & Neville.)

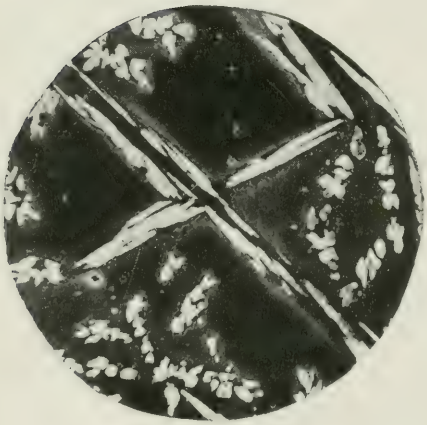
Etchant: Acid ferric chloride.

(Cu = 77·5 ; Sn = 22·5.)

Fig. 450.—Chilled from 558° C. Separation of α crystals (white) from uniform β solution. (× 18.)

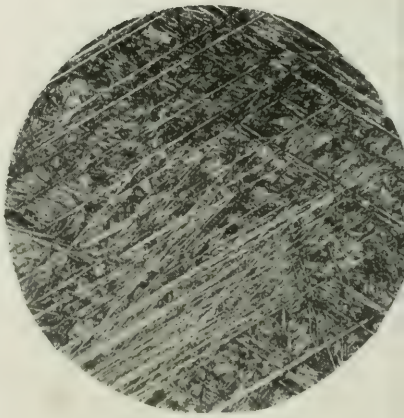
(Cu = 76·7 ; Sn = 23·3.)

Fig. 451.—Chilled from 470° C. Dark α, complex light eutectoid. (× 18.)



(Cu = 76·7 ; Sn = 23·3.)

Fig. 452.—Chilled from 530° C. Newly-formed light α in dark uniform β. (× 18.)



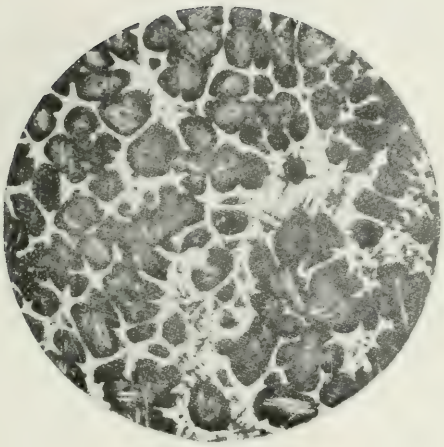
(Cu = 76·7 ; Sn = 23·3.)

Fig. 453.—Chilled from 675° C. Incipient decomposition of uniform β solutio showing striations. (× 18.)

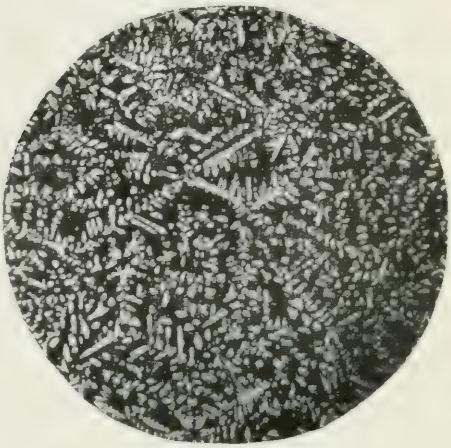
BRONZES (*cont.*).

(Heycock & Neville.)

Etchant: Acid ferric chloride.



(Cu = 74·5 ; Sn = 25·5.)
Fig. 454.—Chilled from 750° C.
Dark primary crystals of β.
(× 44.)



(Cu = 72·35 ; Sn = 27·65.)
Fig. 455.—Chilled from 450° C.
White δ in a complex eutectoid.
(× 250.)

(Cu = 72·35 ; Sn = 27·65.)
Fig. 456.—Chilled from 731° C.
Dark primary β in a tin rich matrix.
(× 18.)

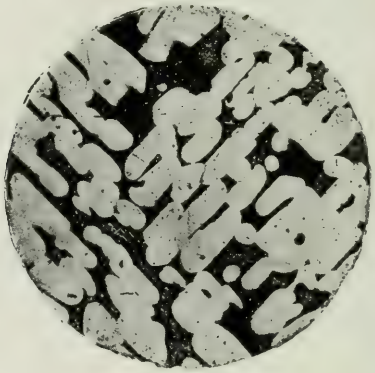
(Cu = 64·85 ; Sn = 33·15.)
Fig. 457.—Chilled from 590° C.
Dark η (Cu_3Sn), white δ.
(× 45.)

BRONZES (*cont.*).

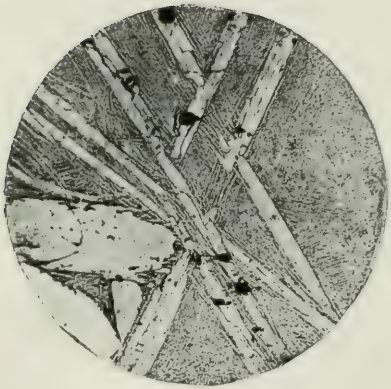
(Heycock & Neville.)

Etchant: Acid ferric chloride.

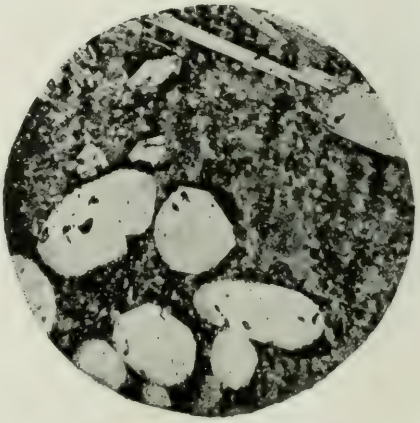
(Cu = 52·1 ; Sn = 47·9.)
Fig. 458.—Chilled from 676° C.
Primary γ.
(× 45.)



(Cu = 46·65 ; Sn = 53·35.)
Fig. 459.—Primary η (Cu_3Sn).
After annealing at 445° C. for 70 hours.
(× 45.)



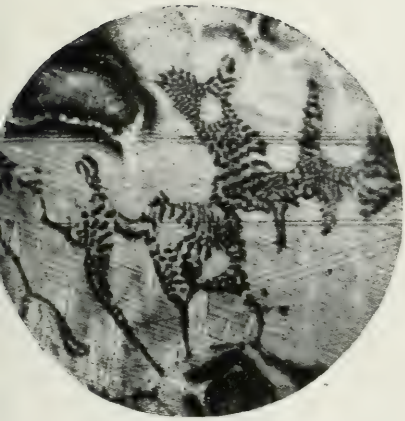
(Cu = 42·5 ; Sn = 57·5.)
Fig. 460.—Chilled from 600° C.
Primary η (Cu_3Sn).
(× 18.)



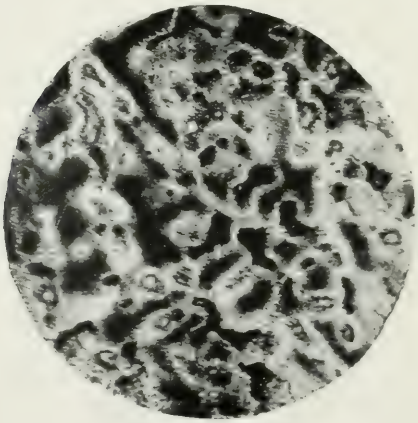
(Cu = 8·7 ; Sn = 91·3.)
Fig. 461.—Annealed for 21 days at 350° C.
Two types of ζ crystals in a eutectic.
(× 45.)

BRONZES (*cont.*).

(Cu = 30; Sn = 70.)
FIG. 462.—Slowly cooled.
Etchant: Hydrochloric acid.
(× 200.)



(Cu = 82; Sn = 18; Pb = trace.)
FIG. 463.—Phosphor bronze.
Etchant: Ammoniacal copper solution.
(× 200.)



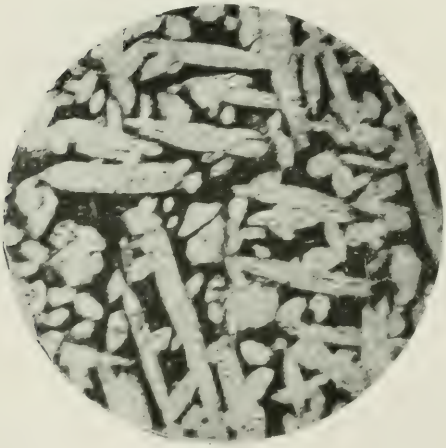
(Cu = 80·1; Sn = 9·5; Pb = 10; Zn = 0·9.)
FIG. 464.—Lead bronze.
Black particles of lead.
Etchant: Ammoniacal copper solution.
(× 100.)

ALUMINIUM BRONZES.

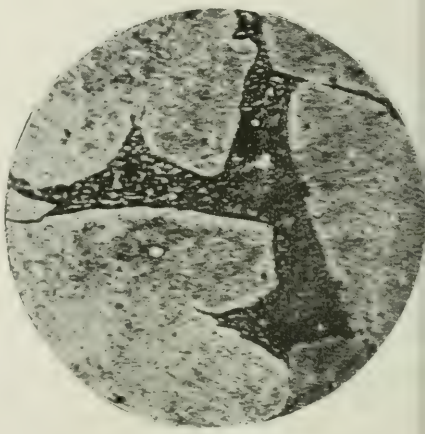
Etchant: Acid ferric chloride.

(Cu = 90·8; Al = 9·2.)
FIG. 468.—Annealed for 4 hours at 800° C.
Polyhedral α, bands of β.

(Cu = 89·5; Al = 10·5.)
FIG. 469.—$\alpha + \beta$.
(× 100.)



(Cu = 90·2; Al = 9·8.)
FIG. 470.—Light α, dark β.
(× 100.)



(Cu = 90·2; Al = 9·8.)
FIG. 471.—α solid solution and eutectoid β.
(× 200.)

Annealing.—It has already been shown that annealing renders the α solid solution homogeneous (Figs. 107, 108, Pl. XIII. *cont.*), produces a polygonal structure, and, where required, as in alloys bordering on the $\alpha + \delta$ area, causes the disappearance of δ, the presence of which denotes that the alloy is not in equilibrium.

Under these circumstances annealing softens the metal and increases the elongation.

Annealing is also useful in the case of the $\alpha + \delta$ alloys, rendering the distribution of the δ constituent more uniform, and thereby improving the frictional qualities of the alloy. The annealing of cold-worked material produces effects analogous to those described in the case of the brass α solid solution.[1]

Relation between the Diagram and the Industrial Uses.—The α solid solution being very ductile, alloys of this constitution are widely used for medals and coinage (Cu = 90 to 96 per cent., frequently with 1 per cent. zinc).

When alloys possessing the maximum strength and minimum brittleness are required, the composition usually closely approaches that at which the δ constituent first makes its appearance; gun-metal, formerly used for ordnance, contained 10 per cent. tin. Frequently gun-metal for machining purposes is used in the form of round rolled bar containing 88–92 per cent. copper, the metal in this condition possessing superior qualities to the cast state. The comparative figures are given:

Cast state, alloy containing 8 per cent. Sn:—

Ult. st. = 14·5 tons E = 5·05 tons Percentage elongation = 10

Rolled and annealed, the same alloy gave:—

Ult. st. = 24·0 tons E = 9·5 tons Percentage elongation = 67

Various articles, notably gear wheels, require certain anti-frictional qualities (resistance to wear) combined with comparatively high strength. The alloys containing mostly α with a little δ satisfy these requirements, the composition of such alloys being 87–90 per cent. Cu.

Articles subject to frictional loads, bearings, bushes, etc., derive their good qualities from the presence of the δ constituent. The pressure at which they will work satisfactorily is dependent, other conditions being equal, on their δ content, and therefore on the amount of tin they contain; but the brittleness and the working difficulties increase with the δ content. The bearing bronzes are therefore divided into several classes, according to the loads to be supported; very hard containing 78–82 per cent. Cu, hard bearing

[1] A research on the results to be obtained by annealing a bronze containing 6 per cent. Sn after cold-work has been carried out by Goerens and Dumont (*Rev. de Met.*, vol. xi. *cont.*, p. 30, 1914).

bronzes containing 82–84 per cent. Cu, and soft bronzes containing 84–88 per cent. Cu. As regards wearing qualities, the experiments of Nusbaumer and one of the authors [1] have shown that these increase in proportion to the amount of δ present in the alloy.

Bell-metal used for church bells, etc., owes its sonorous qualities to the δ constituent or Cu_3Sn present; it contains at most 80 per cent. Cu, and frequently only 50–60 per cent. Cu.

The ancient mirror bronzes also owed their hardness and high polish to the presence of Cu_3Sn; they contained approximately 65 per cent. Cu.

4. Special Bronzes

The theory given in the case of the special brasses is equally applicable to the special bronzes, but has not been so thoroughly investigated for these alloys. The principal classes of these alloys will be described.

Zinc Bronzes

Zinc is very frequently added to a copper-tin alloy. Such additions are made for various reasons: to decrease the cost; facilitate melting, since the liquidus is lower. But in certain instances the presence of zinc is harmful to the mechanical properties.

One of the authors has shown, with Révillon,[2] that zinc adds its effect to copper as regards the constitution of an alloy. Thus the bronzes of compositions:

$$Cu = 90 \quad \text{and} \quad Sn = 10$$
$$Cu = 86 \qquad Sn = 10 \qquad Zn = 4$$

have similar microstructures.

Therefore the addition of zinc to a bronze produces the following effects: decreases the δ constituent and increases the amount of α constituent.

Thus it will diminish the strength and anti-frictional qualities and will increase, to a certain extent, the elongation and the possibility of cold-working the material.

The quantity of zinc in commercial bronzes may be as great as 8–10 per cent. zinc.

Lead Bronzes—Plastic Bronzes

The addition of lead to a bronze serves a double purpose—it gives a more easily worked alloy, as with the brasses, and improves the anti-frictional qualities (wear). This is owing to the fact that it remains in the isolated state in the alloy.

Lead is but very slightly soluble in the α solution; it remains

[1] Portevin et Nusbaumer, *Rev. de Met.*, vol. ix. p. 61, 1912.
[2] Guillet and Révillon, *Rev. de Met.*, vol. vii. p. 429, 1910.

isolated in the form of minute globules scattered more or less uniformly throughout the mass.

Formerly the lead content of bronzes rarely exceeded 8–10 per cent. lead. In modern practice alloys of approximately the following composition are in general use :

$$Cu = 64 \qquad Pb = 30 \qquad Sn = 5 \qquad Ni = 1$$

The object of the 1 per cent. Ni is to facilitate the uniform distribution of the lead throughout the mass. The effect of the nickel does not appear to be definitely proved, and the homogeneity of the alloy would seem to be much more dependent on the casting conditions. Microscopical examination after simple polishing shows the lead as minute globules or plates, as in the brasses (Fig. 464, Pl. LXXXVI., p.233).

Phosphor Bronzes

The phosphor bronzes must be classified into two classes : those which after manufacture only contain traces of phosphorus (less than 0·01 per cent. P), and those containing appreciable quantities ranging from 0·01 to 0·3 per cent. phosphorus.

In the first case, the phosphorus merely serves as a deoxidising agent. It has been shown that copper oxidises during melting and that it dissolves the oxide, Cu_2O, in the molten state. This oxide is not soluble in solid copper, and therefore exists as a form of slag (see p. 204). In bronzes, according to Heyn and Bauer, it forms tin oxide, SnO_2. Phosphorus, added in the form of phosphor-copper or phosphor-tin containing 10 per cent. or 15 per cent. phosphorus, reduces the oxide present, Cu_2O or SnO_2, and forms a phosphate which separates easily in the form of slag.

Prepared in this manner, the metal possesses greatly improved properties, the elongation and elasticity (impact figure) being particularly improved.

In bronzes containing small quantities of phosphorus, the phosphorus forms a separate constituent ; it will be found in the $\alpha+\delta$ eutectoid in the form of Cu_3P. It increases the hardness, but at the same time increases the brittleness (Fig. 463, Pl. LXXXVI.).

5. Copper-Aluminium Alloys

The copper-aluminium series includes two types of alloys of commercial interest :

1. The alloys rich in copper known as aluminium bronzes, and which, in many respects, resemble the brasses ; they contain above 88 per cent. Cu.

Between 88 per cent. Cu and 20 per cent. Cu (approximate) the alloys are extremely brittle.

2. The alloys rich in aluminium, utilised because of their low density ; they contain above 90 per cent. aluminium.

The two extreme limits of the Cu-Al diagram will therefore be considered.

Diagram.—Copper rich section.—*Liquidus.*—At the copper end the liquidus is formed of an inclined but almost straight line, AB, commencing from the melting point of copper, and by a curve BCD showing a maximum at the point C. The α solid solution is deposited along AB ; another solid solution, β, along BCD.

Solidus.—The corresponding solidus consists of an inclined, practically straight section Aa, along which the solidification of the α solution is completed, an horizontal aB, and two sections of curves BC and CD, touching the maximum C, and nearly coinciding with the liquidus. Therefore the point C corresponds to a compound or else to the compound Cu_3Al entering into solid solution.

There is not, correctly speaking, a eutectic at the point B, since the eutectic horizontal only exists on one side of this point.

Transformation Lines.—The β solid solution, the limits of composition of which vary with the temperature, undergoes changes on cooling, liberating α along Bm and γ along Dm, the point m corresponding to the eutectoid $\alpha+\gamma$ at a temperature of 575° C.

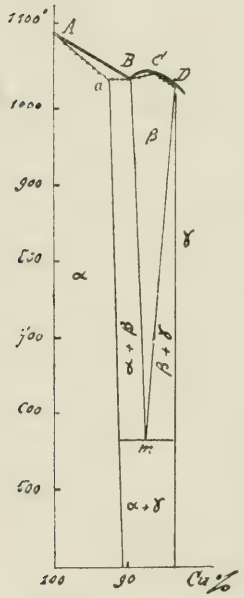


FIG. 466.—Section of copper - aluminium diagram (copper-rich section).

Constituents (Pls. LXXXVII. [p. 233] to XC. [p. 238]).—It will be observed that at ordinary temperature the alloys rich in copper are of the following constitution :

1. Between 100 per cent. and 92·5 per cent. Cu : α solid solution.

2. Between 92·5 per cent. and 86 per cent. Cu : α solid solution and γ solid solution and their eutectoid, frequently termed β, which is present in proportions corresponding to the copper content. Comparison may be made with the copper-zinc diagram. In this case the eutectoid is clearly visible under the microscope, which is the opposite to what has been found with the brasses.

The same etchants may be used for these alloys as were suggested for the brasses.

The α constituent when viewed under the microscope without etching is of a golden yellow colour. It is slightly coloured by ferric chloride, and after etching appears of various shades tending towards reddish-yellow.

The $\alpha+\gamma$ eutectoid may be clearly resolved when the alloy

has been slowly cooled (Figs. 480, 481, Pl. XC.); it then appears, as stated by one of the authors,[1] either in the lamellar form resembling pearlite in steels or with a reticular distribution.

The γ constituent is coloured brown by prolonged etching with acid ferric chloride in aqueous or alcoholic solution, and appears as areas of regular outline in cast alloys (Fig. 482, Pl. XC.).

According to the temperature and conditions of quenching, the quenched alloys show a partial or complete martensitic or acicular structure, which probably bears a similar relation to the β constituent as martensite bears to the solid solution (γ iron-carbon) (Figs. 476, 478, Pl. LXXXIX., p. 238).

Aluminium-Rich Section.—*Liquidus.*—Starting from pure aluminium, the liquidus consists of a curve GF corresponding to the separation of a solid solution η, and another branch FE more nearly horizontal along which the compound Al_2Cu solidifies. The eutectic point F corresponds to a temperature of 540° C. and a copper content of 33 per cent. Cu, the point E corresponds to the compound Al_2Cu, and the curve at this point is tangential to the horizontal.

Solidus.—This consists of a curve G*g* and a horizontal *eg* passing through the point F. Therefore the point F corresponds to the eutectic point of the solution η and the compound Al_2Cu.

Transformation Lines.—The area corresponding to the η solid solution is outlined by the curve gg_1. These alloys show no transformations.

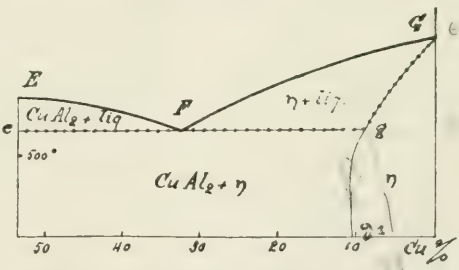


FIG. 467.—Copper-aluminium diagram (aluminium-rich alloys).

Constituents (Pl. XCL.).—At atmospheric temperature the alloys containing 0 per cent. to 11 per cent. Cu consist of a single solid solution; those containing between 11 per cent. and 53 per cent. of copper of this solid solution and the compound Al_2Cu together with the eutectic of these two constituents (Figs. 483–485, Pl. XCI., p. 239).

The best etchant for these alloys is dilute potassium hydrate, as described in Chap. I.

The η solid solution shows very little heterogeneity. The compound Al_2Cu appears as clearly defined crystals.

Relation between the Diagram and the Mechanical Properties at Ordinary Temperatures—*Copper-rich Alloys.*—The curves (Fig. 487) show the ultimate strength, the elastic limit, and the percentage elongation of rolled and annealed alloys.

[1] Portevin, *Inter. Zeit. für Met.*, vol. x. p. 948, 1913.

It will be observed that the ultimate strength and the elastic limit increase in proportion to the aluminium content, whereas the elongation reaches a maximum at a composition which approximately corresponds to the appearance of eutectoid. When over 10 per cent. Al is present the alloys become brittle, owing to the presence of free γ solution.

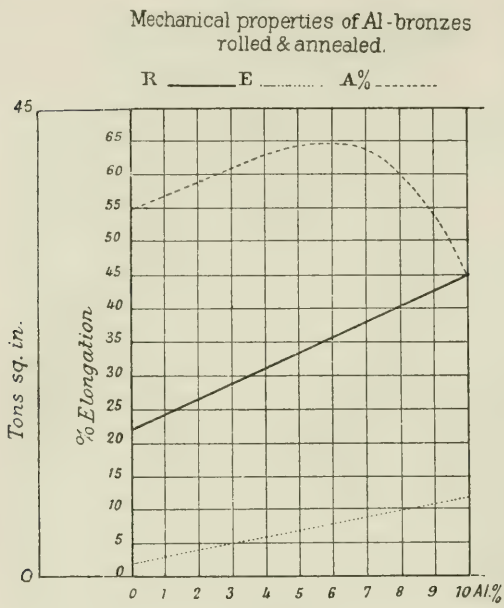


FIG. 487.

Thus the α solid solution is more malleable and stronger the greater the aluminium content, and in this respect differs from the α solution of the copper-zinc series, which possesses a maximum malleability with 70 per cent. Cu; the γ solution causes brittleness, and when it is present in the free state the alloys are brittle.

Alloys Rich in Aluminium.—The η solid solution is malleable and greatly resembles aluminium. However, whereas the ultimate strength is increased, the elongation is decreased.

The following figures are typical for rolled and annealed material:

	Ult. strength	Percentage elongation.
Aluminium 99·5 per cent.	7·6 tons	31
Aluminium *cont.* 3 per cent. Cu ..	12·3 tons	12
Aluminium *cont.* 6 per cent. Cu ..	12·6 tons	10

On the appearance of the compound Al_2Cu, the hardness and brittleness increase, even when the Al_2Cu is present in the eutectoid.

Relation between the Diagram and Treatment.—*Mechanical Treatment—Copper-rich Alloys.*—The malleable α solid solution may be rolled both hot and cold.

The β solid solution, stable at high temperature, can be forged, whereas the presence of the brittle γ solid solution renders rolling impossible.

It follows that it is possible to roll, both hot and cold, all alloys containing over 92 per cent. Cu, and that alloys containing between 88 per cent. and 92 per cent. Cu may be hot-rolled at a temperature above 550° C. but below the solidus (approximately 1050° C.).

It will be observed that, owing to the position of the solidus,

ALUMINIUM BRONZES (*cont.*).

Etchant: Acid ferric chloride.

(Cu = 90·2; Al = 9·8.)

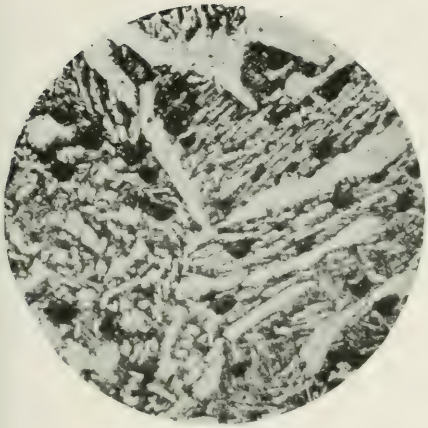


FIG. 472.—Chilled from 750° C.
Light α + dark β.
(× 50.)

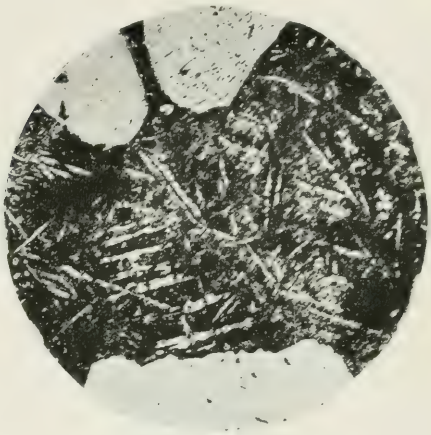
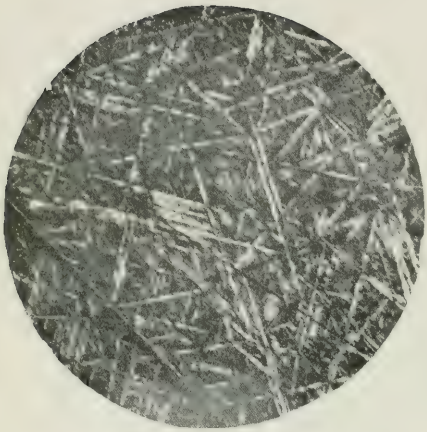


FIG. 473.—Chilled from 600° C.
Showing secondary α due to the decomposition of β.
(× 200.)

FIG. 474.—Chilled from 900° C.
β constituent with still a little α.
(× 50.)

FIG. 475.—Chilled from 950° C.
Nearly pure β.
(× 200.)

ALUMINIUM BRONZES (*cont.*).



(Cu = 88·1 ; Al = 11·9.)
FIG. 476.—Chilled from 750° C.
Martensitic structure.
Etchant : Ammoniacal copper solution.
(× 200.)

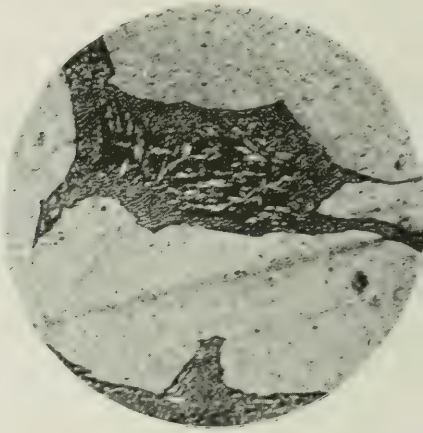
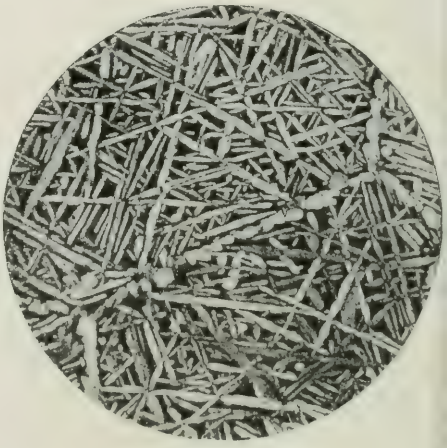


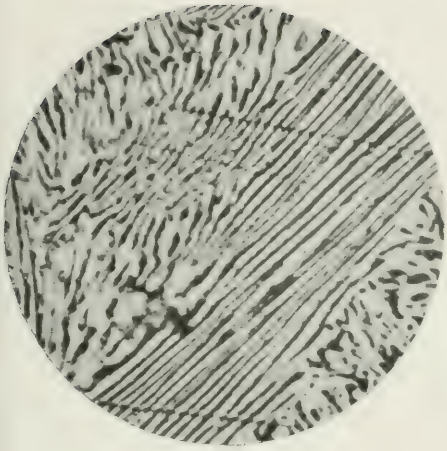
FIG. 477.—Chilled from 600° C. and reheated to 300° C.
Etchant : Acid ferric chloride.
(× 200.)

(Cu = 90 ; Al = 10·0.)
FIG. 478.—Chilled from 900° C.
Etchant : Acid ferric chloride.
(× 200.)



(Cu = 90 ; Al = 10.)
FIG. 479.—Chilled from 900° C. and reheated to 600° C.
Etchant : Acid ferric chloride.
(× 200.)

ALUMINIUM BRONZES (*cont.*).



IG. 480.—Lameller eutectoid in an aluminium bronze slowly cooled.
Etchant: Acid ferric chloride in alcohol.
(× 900.)

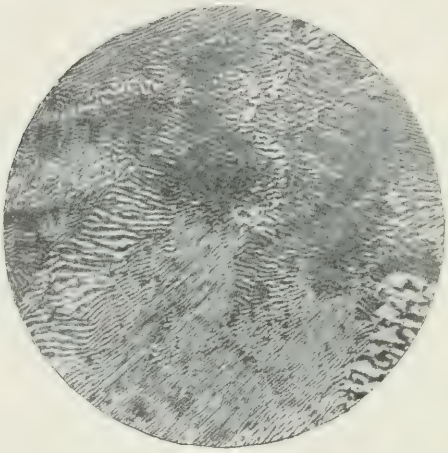


FIG. 481.—Pure eutectoid.
Etchant: Acid ferric chloride in alcohol.
(× 580.)

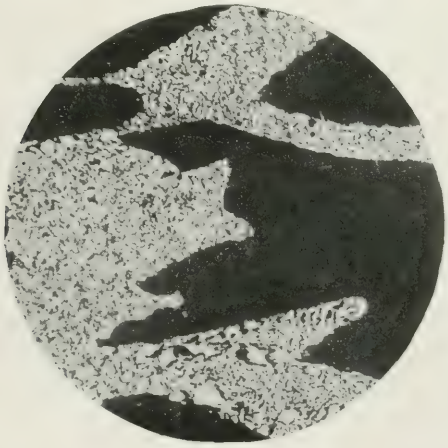
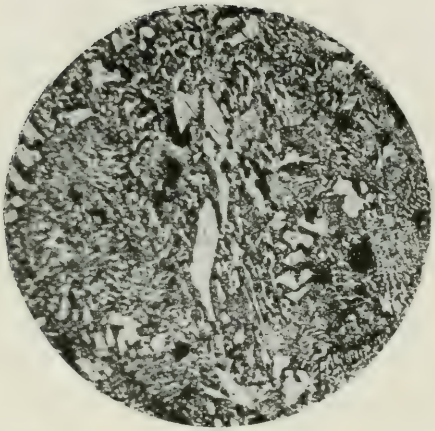


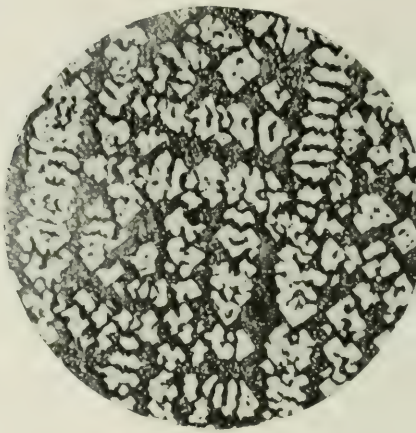
FIG. 482.—Hypereutectoid copper-aluminium.
Alloy slowly cooled, black γ and resolved β eutectoid.
Etchant: Acid ferric chloride in alcohol.
(× 60.)

COPPER ALUMINIUM ALLOYS.

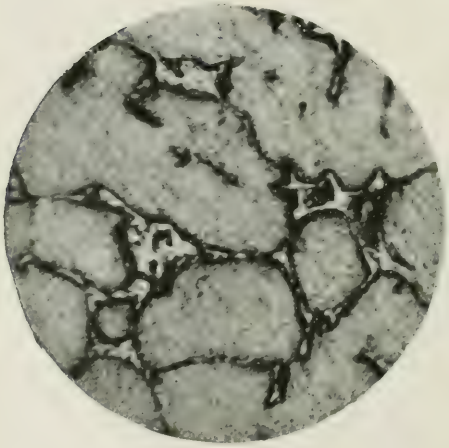
Etchant: Hydrochloric acid (dilute).



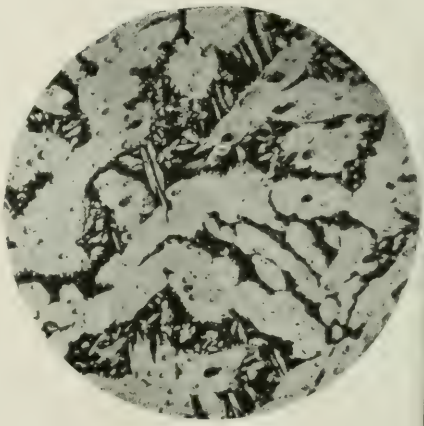
(Al = 65; Cu = 35.)
FIG. 483.—Constituent η + eutectic ($\eta + Al_2Cu$).
(× 50.)



(Al = 60; Cu = 40.)
FIG. 484.—Constituent Al_2Cu + eutectic ($\eta + Al_2Cu$).
(× 200.)



(Al = 95; Cu = 5.)
FIG. 485.—Constituent η + a small amount of eutectic.
(× 100.)



(Cu = 90·2; Al = 9·8.)
FIG. 486.—Chilled from 600° C. Primary and secondary $\alpha + \beta$.
(× 50.)

the range of temperature suitable for hot-working is very much greater than in the case of brass. This is of importance in the commercial manufacture of these alloys.

Aluminium-rich alloys.—The alloys consisting of the η solid solution may be treated in a similar manner to aluminium, but the presence of the compound Al_2Cu renders the metal unworkable.

Heat Treatment.—*Copper-rich Alloys—Quenching.*—The diagram indicates that quenching is applicable to alloys containing 92 per cent. to 88 per cent. Cu and defines the quenching temperature.

When such an alloy is submitted to a series of quenchings at increasing temperatures above the transformation temperature, needles at first appear in the eutectoid; these needles then spread more and more over the surface of the specimen until finally there is found a very clearly defined martensitic structure (Figs. 476, 478, Pl. LXXXIX.).

If such a quenched aluminium bronze is tempered, analogous results will be obtained to those described for steels; it must, however, be observed, as shown by Arnou and one of the authors,[1] that the separation of the pro-eutectoid α constituent occurs in the form of needles producing a Widmanstaetten structure (Fig. 479, Pl. LXXXIX.).

Quenching, producing the martensitic structure, gives, as in the case of steel, increased ultimate strength and elastic limit, but decreases the elongation and impact figure.

Example: Alloy composition: Cu=89·1, Al=10·1:

	Ult. strength.	Percentage elongation.
As cast	15·75 tons	20·0
Quenched from 750° C. ..	21·39 tons	17·5
Quenched from 850° C. ..	22·27 tons	7·0

Annealing.—Annealing gives similar results to those obtained with the brasses. It renders the cast α solid solution homogeneous and thereby gives improved mechanical properties to the material, notably an increase in elongation. But, and this is a distinct difference, commercial annealing brings about the resolution of the eutectoid with the aluminium bronzes, and this does not occur with the brasses. The effect of tempering has been described.

Aluminium-rich Alloys.—These alloys are not quenched, but those alloys bordering on the limits of the η solid solution area are slightly altered by quenching, and the elongation is slightly increased owing to the disappearance of the Al_2Cu.

Annealing renders the η solution more uniform, but it is practically homogeneous after simple casting.

Relation between the Diagram and the Industrial Uses.—The alloys rich in copper consisting of a single solid solution are extremely malleable and may be used for stampings, etc. It should be noted

[1] Portevin and Arnou, *C. R.*, cliv., 1912.

that the colour of these alloys, reddish yellow with the lower aluminium contents, becomes greenish yellow with 8 per cent. aluminium. The alloys consisting of α solution and eutectoid are of golden colour; they possess very remarkable mechanical properties and are extremely resistant to chemical corrosion.

The most usual type of alloy: Cu=90, Al=10, discovered by Henry Sainte-Claire Deville and known under his name, is used for the manufacture of knives and forks, plates and dishes, cheap jewellery, pump rods, valve spindles, certain types of springs, etc.

Undoubtedly this alloy will be more widely used for engineering purposes in the future. The alloys rich in aluminium, consisting of the η solid solution, may often be substituted for aluminium with advantage, and in most instances, without appreciably increasing the density. However, it should be observed that these alloys are rather more readily attacked by moist air than commercially pure aluminium.[1]

6. **Cupro-Nickel Alloys, Nickel Silvers** (Cu-Ni-Zn)

Alloys of Copper and Nickel.—These alloys are known as cupro-nickels.

Diagram.—The liquidus L consists of a single curved section AB, the solidus S is of similar form. The copper-nickel alloys are therefore entirely miscible and form one series of solid solutions (Fig. 488).

The only transformation points are the magnetic transformations which are shown on an enlarged scale by CD and CD′. It will be observed that the only magnetic alloys at ordinary temperatures are those containing above 58 per cent. nickel (Fig. 488). The separation of the curves indicates the hysteresis.

Other Physical Properties.—The electrical conductivity curve MPQ (Fig. 488) is additional proof of the existence of a single solid solution.

[1] The special aluminium-bronzes ought next to be considered, but the examination of these series of alloys is not sufficiently advanced to be considered on the equivalent coefficient basis. However, it is necessary to mention the remarkable work of Carpenter and Edwards (*Inter. Zeit. Metall.*, vol. ii. p. 209, 1912, and *Rev. de Met.*, vol. x. p. 427, 1913), which has traced out the diagram of the Al-Cu-Sn system, and several microscopical observations of Robin, on various special aluminium bronzes. One of the authors has shown (Guillet, *Comptes rendus de l'Academie des Sciences*) that nickel gives an apparent content which is considerably higher than the real content. The aluminium bronzes containing iron may be examined, as they exhibit very remarkable mechanical properties. The figures for these alloys are in the cast condition:

Composition.	Ult. strength.	E.	Percentage elongation.	Percentage reduction of area.
9·16 per cent. Al+3·2 per cent. Fe	38 tons	17·7	25	27·0
5·47 per cent. Al+3·6 per cent. Fe	32·4 tons	11·9	28	31·7

Refer also to the work of Read and Greaves on the Cu-Al-Ni alloys (*Inst. of Metals*, March, 1913).

Constituents (Pl. XCII.).—The single solid solution appears very heterogeneous in the cast state and might be mistaken for two constituents (Fig. 490, Pl. XCII.). After annealing, it is homogeneous and possesses a polygonal structure.

The most satisfactory etchants are acid ferric chloride and ammoniacal copper solution.

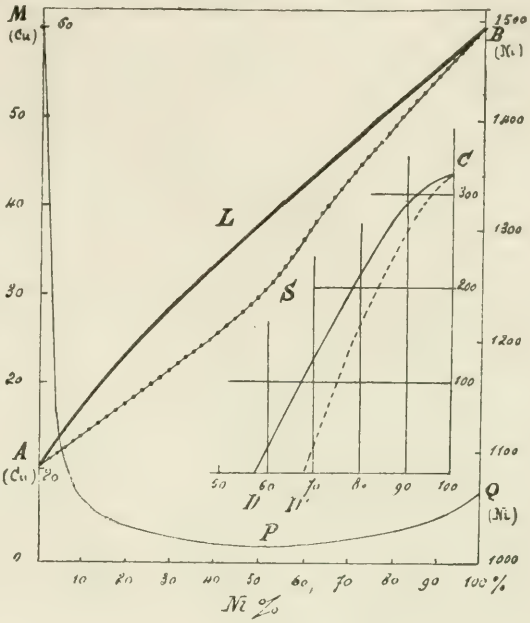


FIG. 488.—Copper-nickel diagram (Kurnakow and Zemczuzny).

Relation between the Diagram and the Mechanical Properties at Ordinary Temperature.—According to the diagram, the properties should be represented by a continuous curve showing a maximum value (see Chap. III., p. 106). Kurnakoff has determined the Brinell hardness numbers (10 mm. ball, 500 kilo. load) of the complete series of these alloys (with 2 per cent. Mn to permit rolling). The hardness increases from pure copper to the alloy containing 45·6 per cent. Ni and then decreases again to pure nickel. One of the authors [1] has shown, in the case of rolled and annealed alloys of varying copper content between 95 per cent. and 70 per cent. Cu, that the ultimate strength, which increases slowly at the commencement, reaches 16 tons sq. in. with 30 per cent. nickel; whereas the elastic limit, which is very low in the alloys of high copper content (1·25–1·9 tons up to 20 per cent. Ni), suddenly increases rapidly (14 tons with 30 per cent. Ni). The elongation drops very rapidly above 10 per cent. Ni.

Relation between the Diagram and Treatment.—*Thermal Treatment.*—None of the alloys is altered by quenching, since the non-magnetic state is not retained by quenching.

Annealing is the only heat treatment of any importance for cupro-nickel alloys. The effect of such treatment on cast metal has already been described—rendering the alloy homogeneous, producing a polygonal structure, the size of which is dependent on the temperature and time of annealing (see analogous examples

[1] Guillet, "Etude industrielle des alliages métalliques," t. ii. p. 1908.

with nickel-silvers, Figs. 489, 491, Pl. XCII.). With suitable time and temperature of annealing there is a distinct improvement in the mechanical properties of these alloys by such treatment.

The annealing of cold-worked metal produces similar results to those results described for brasses.

Relation between the Diagram and Industrial Uses.—The use or application of cupro-nickel alloys is dependent on three main factors: their cost, their colour, and their resistance to corrosion.

The white colour required for most purposes is only found in alloys containing over 20 per cent. Ni. At this composition the elongation is already reduced, but the metal remains sufficiently malleable for most purposes, notably stamping and machining (rifle-bullet cases, tubes, etc.).

Copper-Nickel-Zinc Alloys

These alloys, usually termed nickel-silvers or German-silvers, have recently been systematically examined.[1]

Only the alloys in commercial use will be described. These alloys usually contain: Cu=60–75 per cent., Ni=10–25 per cent., Zn=15–30 per cent. (also lead in alloys for machining), and are formed of an uninterrupted series of solid solutions. They are malleable, and when of high copper content may be considered in a similar manner to the cupro-nickel alloys (Pl. XCII., Figs. 489, 491). Recrystallisation of the cold-worked metal commences at 300° C. when only 7 per cent. Ni is present, but not until 600° C. when the nickel content is 28·6 per cent. Ni (Thomson).

However, a distinct difference will be found as regards mechanical treatment, since the brittleness at high temperature continues until very near the solidus, which is distinctly different to the case of the copper-nickel alloys, where, it is true, the solidus is at a much higher temperature.

These alloys are in general use for the manufacture of various domestic articles—spoons, forks, table requisites, etc. They are also used in the form of wire for electrical resistances.

The following reference tables show the resistance at 0° C. in microhms per centimetre cube and the mean temperature coefficient between 0° and 100° C.

Several of the less important copper alloys have been purposely omitted, as they do not come within the scope of the present volume. These are:

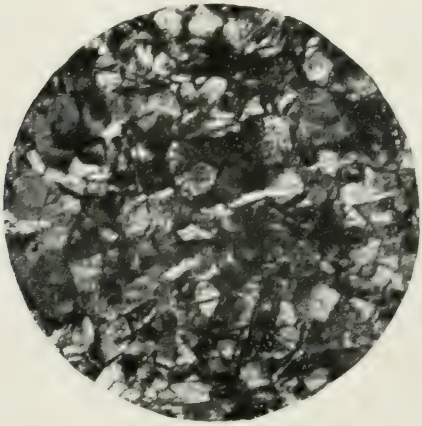
The copper-manganese alloys, used for stay bolts for locomotive fire-boxes, and as additions in the manufacture of bronzes and brasses.

[1] Ref. F. C. Thomson, *Jour. Chem. Soc.*, 1914; *Inst. of Metals*, 1916 and 1917.

CUPRO-NICKELS AND NICKEL-SILVERS.

(Cu = 58 ; Zn = 24 ; Ni = 18.)
FIG. 489.—Nickel-silver as cast.
Composition for castings.
Etchant : Ammoniacal copper solution.
(× 50.)

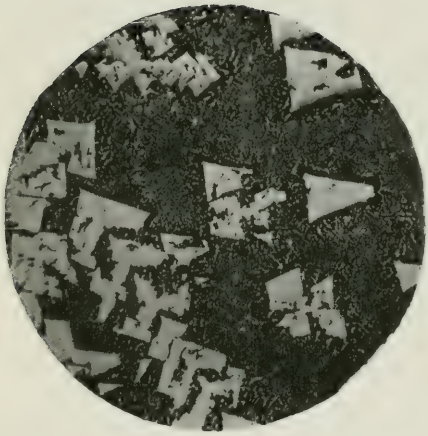
(Cu = 75 ; Ni = 25.)
FIG. 490.—Cupro-nickel as cast.
Etchant : Ferric chloride.
(× 50.)



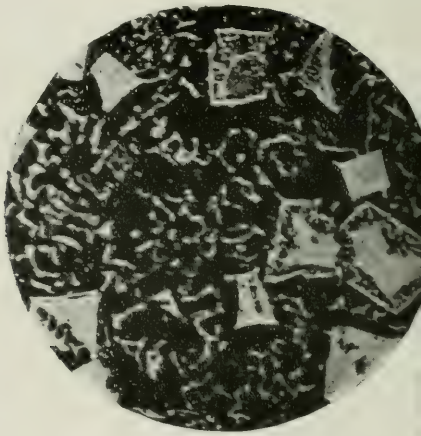
(Cu = 59·68 ; Ni = 18·59 ; Zn = 20·82 ; Fe = 0·40 ; Pb = 0·81.)
FIG. 491.—Rolled nickel-silver.
Etchant : Ammoniacal copper solution.
(× 50.)

BEARING METALS.

Etchant: Dilute hydrochloric acid.



(Sn = 11·6; Sb = 15·50; Pb = 72·8; Zn = trace.)
FIG. 498.—Bearing metal.
(× 50.)



(Sn = 14; Pb = 76; Sb = 10.)
FIG. 499.—Bearing metal.

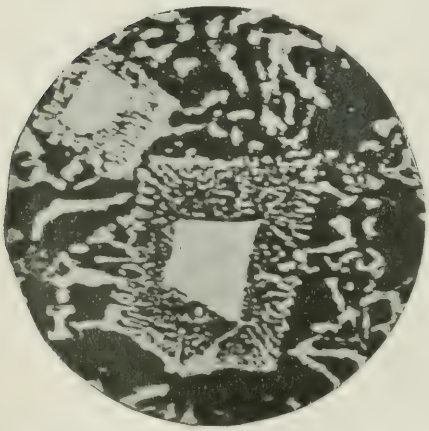


FIG. 500.—Tin-antimony-lead alloy.
Crystals of Sb-Sn surrounded by a binary eutectic.
(× 200.)

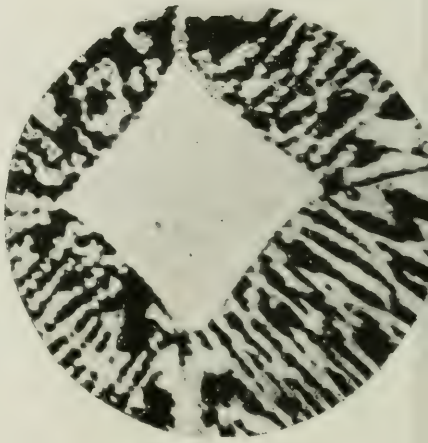
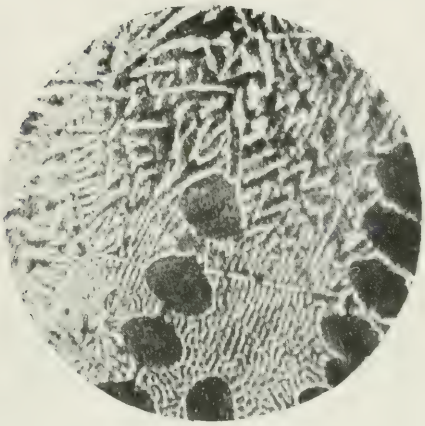


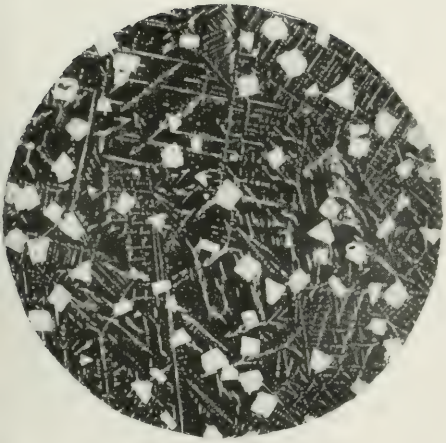
FIG. 501.—The same as Fig. 500 under higher magnification.
(× 400.)

BEARING METALS (*cont.*).

Etchant: Dilute hydrochloric acid.



(Sn = 12; Sb = 8; Pb = 80.)
FIG. 502.—Bearing metal.
(× 200.)



(Sn = 82·23; Sb = 13·6; Pb = 0·77; Cu = 5·58.)
FIG. 503.—Cubes of SbSn compound; needles of CuSn compound in a ground mass of eutectic.
(× 50.)

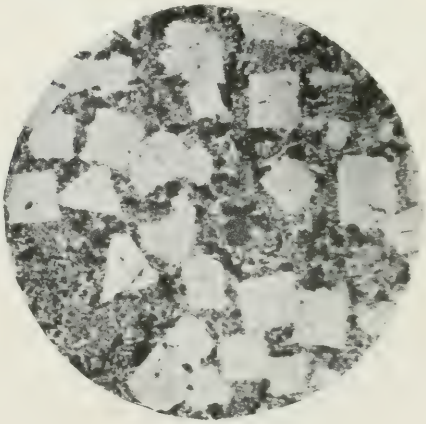
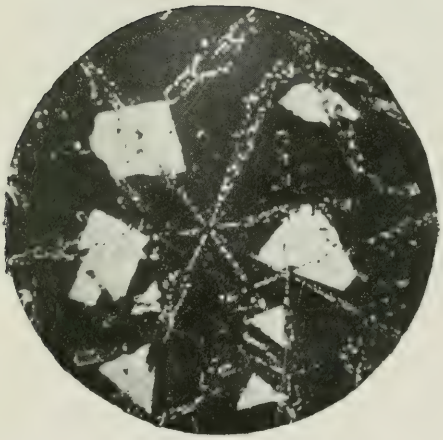


FIG. 504.—Commercial bearing metal. Cubes of SbSn compound, ground mass of lead and eutectic.
(× 50.)

BEARING METALS (*cont.*).

Etchant: Dilute hydrochloric acid.



(Sn = 83; Sb = 5·5; Cu = 11·5.)
FIG. 505.—Bearing metal of commerce.
(× 50.)

(Cu = 5·55; Sn = 83·33; Sb = 11·11.)
FIG. 506.—Bearing metal.
(× 200.)

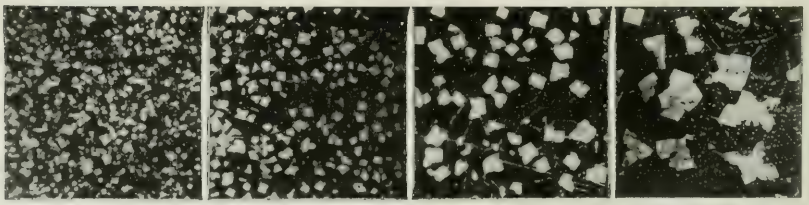


FIG. 507.—Effect of the rate of cooling on the structure of bearing metals.

TABLE I

RESISTIVITY AND MEAN TEMPERATURE COEFFICIENTS (GEORGES MATTER AND SWAN)

Metals.	Microhms per cm. cube.	Mean temp. coef. 0°–100° C.
Platinum (wire 0·025945 cm. diam.)	10·950	0·003529
Gold	2·197	0·00377
Palladium	10·219	0·00354
Silver	1·468	0·00400
Copper	1·561	0·00428
Aluminium 99·0 per cent.	2·563	0·00423
,, commercial (97·5 per cent.)	2·665	0·00435
Iron (Armstrong) A	10·512	0·00544
Nickel	12·323	0·00622
Tin	13·048	0·00440
Magnesium	4·355	0·00381
Zinc	5·751	0·00406
Cadmium	10·023	0·00419
Lead	20·380	0·00411
Thallium	17·633	0·00398

TABLE II

RESISTIVITIES AND MEAN TEMPERATURE COEFFICIENTS AT 15° C. OF THE PRINCIPAL INDUSTRIAL ALLOYS

Alloy.	Microhms per cm³.	Mean temp. coef. 15° C.
Platinum (34), Silver (66)	31·582	0·000243
Platinum (80), Iridium (20)	30·896	0·000822
,, (90), Rhodium (10)	21·142	0·00143
Gold (90), Silver (10)	6·280	0·00124
Aluminium (94), Silver (6)	4·641	0·00238
,, (94), Copper (6)	2·904	0·0038
Copper (97), Aluminium (3)	8·847	0·000897
Hadfield's Manganese Steel (12 per cent.)	67·148	0·00127
Nickel-silver (Cu=60·1; Zn=25·4; Ni=14·0; Fe=0·4)	29·982	0·008273
Silverine (Cu=77; Ni=17; Fe=2; Zn=2; Co=2)	2·064	0·00285
Copper (87), Nickel 6·5), Aluminium (6·5)	14·912	0·000645
Copper (73), Nickel (3), Manganese (24)	47·7	0·00083
Nickeline (Cu=61·6; Zn=19·8; Ni=18·6)	45·0	—
Cupro-nickel (Cu=75; Ni=25)	34·2	0·00019
Rhéotan (Cu=53·3; Zn=16·9; Ni=25·3; Fe=4·5)	52·5	0·00041
Constantan	50·0	—
Cupro-manganese (Cu=70; Mn=30)	100·6	0·00004
Aluminium-bronze (Cu=90; Al=10)	12·31	0·00105
,, ,, (Cu=94; Al=6)	3·2	—

The copper-silicon alloys, used in the form of wire when of low silicon content, and for adding to various other alloys during manufacture.

The copper-vanadium and copper-iron alloys are very little used.

Bearing Metals

The terms "bearing metal," "white metal," and even "white bronze" are used for the alloys employed in the manufacture of

bearings and articles to withstand frictional loads. The principal types of these alloys are:

1. Binary alloys: lead-antimony.

2. Ternary alloys: lead-tin-antimony, lead-tin-copper (lead bronzes or plastic bronzes already described), lead-tin-bismuth.

3. Quaternary alloys: lead-tin-antimony-copper.

As the complete examination of all these series of alloys has not yet been made, and since, in any case, such an examination is not within the scope of the present volume, the description will be confined to the antimony-lead alloys.

Then, in order that certain conclusions may be drawn for the ternary and quaternary alloys, the constitution of the following binary systems will be briefly considered: lead-tin, lead-copper, tin-antimony, and finally a short examination of a typical ternary system before passing to the microscopical examination of typical commercial bearing metals.

Lead-Antimony Alloys

Diagram.—The liquidus consists of two curves cutting each other at the composition 13 per cent. Sb, and a temperature of 248° C. The solidus consists of a horizontal line passing through the junction of the solidus curves and extending to the extreme limits of the diagram (pure metals) (Fig. 492). Lead and antimony do not form solid solutions.

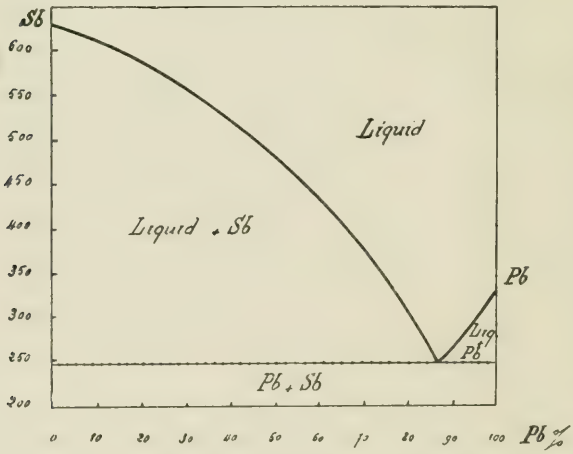


FIG. 492.—Lead-antimony diagram (Gontermann).

Constituents.—The lead-antimony alloys consist of lead and antimony and their eutectic, which corresponds to an antimony content, 13 per cent. Sb. Up to this composition free lead is present, and above it clearly defined crystals of antimony (Fig. 86, Pl. X., p. 22), which increase as the antimony content increases.

Relation between the Diagram, Properties, and Uses.—Lead being malleable, and antimony extremely brittle, the alloys become less and less malleable as the antimony content increases. They never become really brittle until the eutectic composition is exceeded, when they contain crystals of free antimony.

The anti-frictional qualities of these alloys are due to the presence of the antimony crystals, whilst the eutectic forms a plastic matrix to support these crystals, and enables a proper bearing surface to be obtained.

Therefore, if alloys similar to lead but of rather greater rigidity are required, as in the manufacture of accumulators, alloys containing free lead are used (6–8 per cent. Sb). If great hardness or good frictional qualities (wear, etc.) under high pressures are required, then the alloys containing free antimony must be employed (20–40 per cent. Sb in certain type metals, 14–20 per cent. Sb for bearing metals).

Lead-Tin Alloys

Diagram (Fig. 493).—The liquidus consists of two curves cutting each other at the composition, 64·1 per cent. Sn, at a temperature of 181° C.

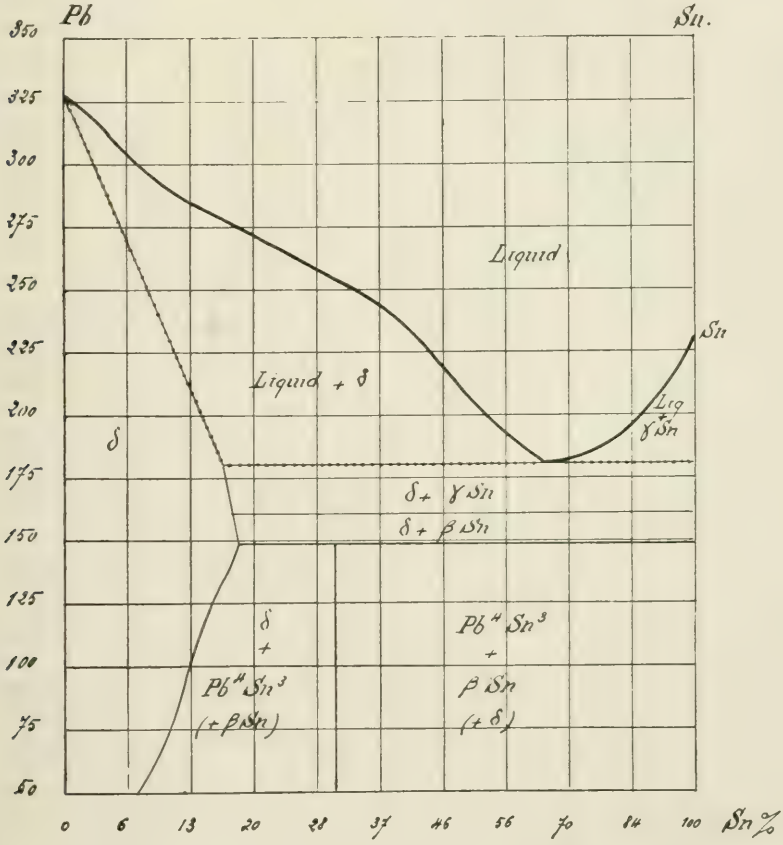


FIG. 493.—Tin-lead diagram (Rosenhain and Tucker, Dogens).

The solidus consists of an horizontal line passing through this temperature, 181° C., finishing on the one side with pure tin and on

the other side at a composition of 16 per cent. Sn, and a curve joining this point with the melting point of lead.

Therefore lead and tin form a solid solution in which the tin content varies with change of temperature, the content at ordinary temperature being 7 per cent. Sn.

The horizontal line may be continued to pure lead if the rate of cooling is sufficiently great.

Further, tin possesses two allotropic modifications. There may be the formation of a compound Pb_4Sn_3, but these transformations occur so slowly that in practice the alloys consist solely of solid solution and tin.

Relation between the Properties and the Constitution.—The solutions at the two extremes exhibit similar properties to lead and tin and are therefore malleable. The same applies to all the alloys. None of them contains any hard crystals. They owe their use either, because they are not attacked by certain liquids (pewter less than 18 per cent. Pb), or to their good casting and working properties (decorative articles containing 40 per cent. lead, lead toys (soldiers) containing 95 per cent. Pb), or to their low melting point (solders containing 60 per cent. Pb which should contain 67 per cent. Pb for the minimum melting point).[1]

Lead-Copper Alloys

Diagram (Fig. 494).—The liquidus consists of a curve commencing from the melting point of pure copper and reaching a temperature

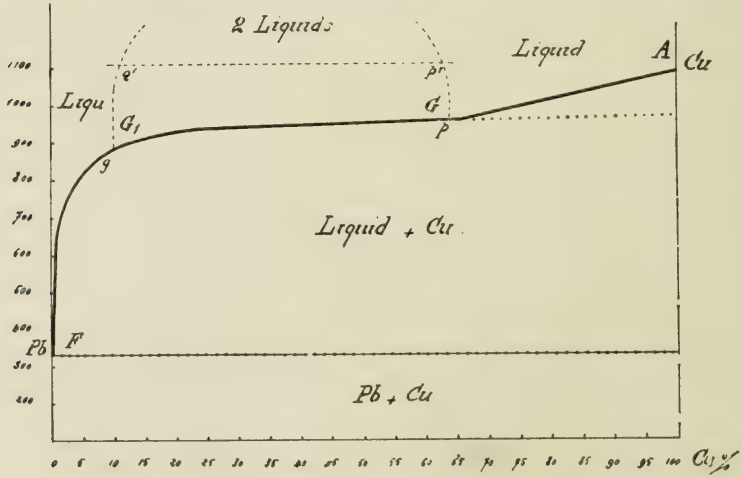


FIG. 494.—Lead-copper diagram (Friedrich and Leroux).

of 950° at a composition corresponding to 40 per cent. lead; an horizontal section continues from this point to the composition

[1] Translator's note: Solders receive special names according to their tin content "Plumbers' solder" contains from 67 per cent. to 50 per cent. lead. "Tinman's

70 per cent. lead, and a curve joins this last point to the melting point of lead.

The solidus consists of an horizontal line passing through the melting point of pure lead.

Copper and lead are partially miscible in the molten state and are non-miscible in the solid state.[1]

Antimony-Tin Alloys

The diagram of these alloys is given, Fig. 495.

The liquidus consists of three sections: AB, BC, and CD, each section corresponding to the separation of a solid solution. The

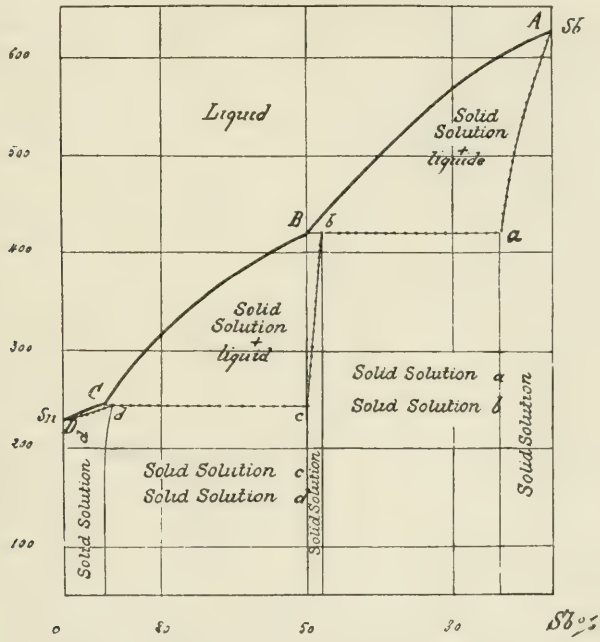


FIG. 495.—Antimony-tin diagram (Williams).

solidus consists of the curve A*a*, the horizontal *ba*, the line *bc*, the horizontal *cd*, and the curve *d*D.

No transformation points need be considered.

At ordinary temperature the constituents are; a solid solution containing 8 per cent. Sn, the compound SbSn forms the solid solutions *b* and *c* and a third solution containing from 0–10 per cent. Sb. The electrical conductivity curve shows the existence of the

solder" of approximately eutectic composition contains 40 per cent. lead. Other solders contain even more tin, and in special instances, as for certain electrical work, up to 90 per cent. tin.

[1] The equilibrium curve of the mixture of the two liquids has recently been plotted by Bogitch, ref. *Rev. de Met.*, vol. xii. p. 655, 1915.

compound SbSn. The δ solution, rich in tin, is the only malleable constituent of the series.

Fig. 110, Pl. XIV. (p. 79), shows the liquid diffusion of these alloys.

Lead-Bismuth and Tin-Bismuth Alloys

Diagram.—The diagrams, Figs. 496, 497, show the constitution of these two classes of alloys.

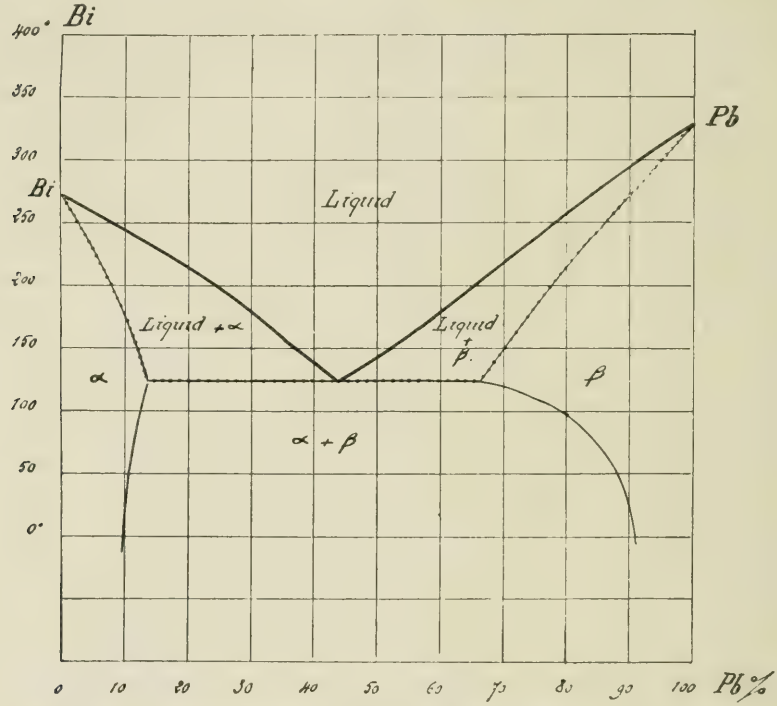


FIG. 496.—Lead-bismuth diagram (Barlow, Kapp, Mazzotto, Shepherd).

The lead-bismuth series contains a eutectic and two solid solutions.

The tin-bismuth series consists of two solid solutions, the one containing 1·3 per cent. Sn, and the other containing 6 per cent. Bi, forming a eutectic.

These alloys have no commercial application and are mentioned in connection with the examination of the lead-tin-bismuth alloys.

Lead-Tin-Bismuth Alloys

Only binary alloys have as yet been considered, but a typical example of a ternary system will now be described.

A simple example will be chosen: the lead-tin-bismuth series investigated by Charpy. In the first instance, it is necessary to show how the results are represented as regards fusibility (Fig. 498).

If in an equilateral triangle, ABC, each apex represents one of the metals considered, then a point M, situated inside the triangle,

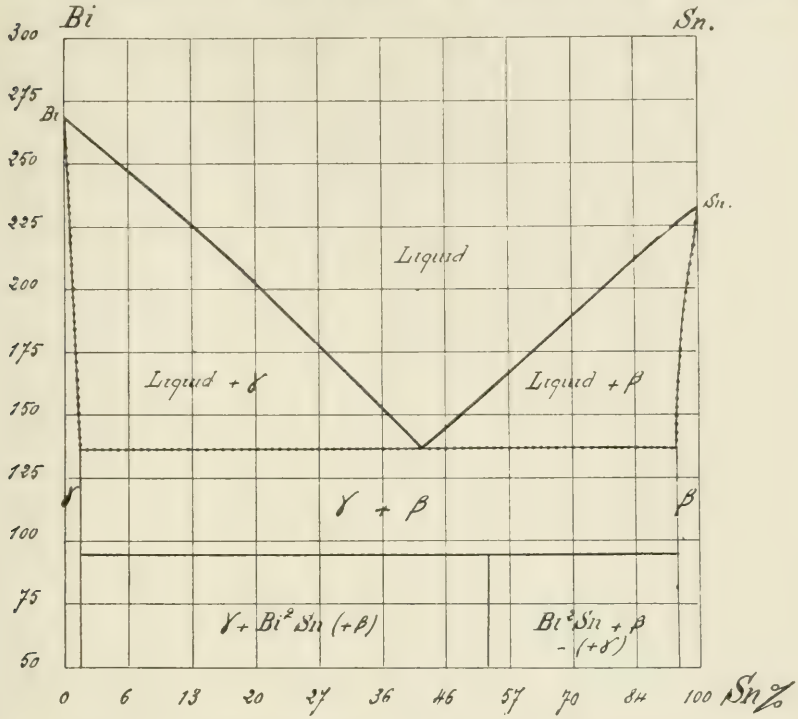


FIG. 497.—Bismuth-tin diagram (V. Lepkowski and Mazzotto).

will represent an alloy containing M*a* of the metal A, M*b* of the metal B, M*c* of the metal C; the sum total M*a*+M*b*+M*c* being constant, the unity basis is taken as 100.

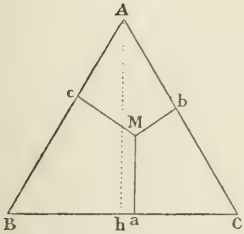
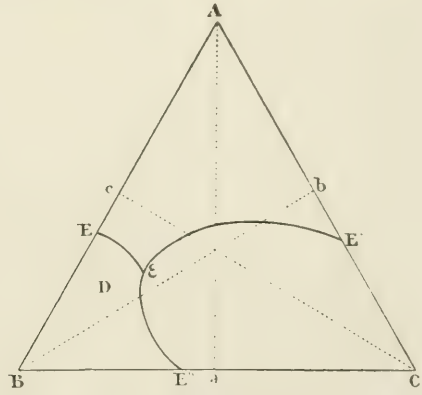


FIG. 498—Diagrammatic representation of the freezing-point surface of a ternary alloy.



498A.—Freezing-point surface of the Pb-Sn-Bi alloys.

The temperatures corresponding to the liquidus, the solidus, and to the transformations at the point M, are found from the

temperature scale perpendicular to the plane of the diagram ; therefore, by varying the position of the point M it will be possible to obtain the surfaces limiting the various sections of the diagram. The lead-bismuth-tin series (Fig. 498A) may be considered as an example.

In the triangle ABC, A represents lead, B bismuth, and C tin. The liquidus consists of three surfaces which cut one another along the three curves $E\epsilon$, $E'\epsilon$, $E''\epsilon$.

E, E′, E″ correspond to binary eutectics ; the point ϵ common to the three curves, corresponds to the ternary eutectic alloy of composition :

Lead	32·0 per cent.
Tin	15·5 per cent.
Bismuth	52·5 per cent.
	100·0 per cent.

Melting point 96° C.

This alloy alone can exist in equilibrium in the liquid state with the three metals, lead, tin, bismuth, if the solid solutions indicated under the binary alloys are excepted.

It is possible to follow the solidification of these alloys, as in the case of the binary alloys. Consider, for example, the alloy the diagrammatic composition of which is shown by the point D ; this alloy will consist of crystals of bismuth, surrounded by the tin-bismuth binary eutectic, which in turn will be surrounded by the ternary eutectic. Microscopical examination readily confirms this constitution (see analogous example shown for Pb-Sn-Sb, Fig. 500, Pl. XCIII., p. 242).

General Structure of Bearing Metals

The subject of frictional wear and the suitability of various alloys to withstand frictional loads in a satisfactory manner is undoubtedly one of the most complex mechanical and metallurgical problems.

Frictional losses, and therefore wear of bearings, are dependent on many factors, not only pressure and the constitution of the bearing metal, but also the speed of revolution, lubrication, etc. It may be said that the selection of a suitable alloy to withstand friction is mainly a question of working conditions.

Under certain circumstances, hardened steel running in hardened steel has given good results ; cast iron running in cast iron, which is suitable in some instances, is not always satisfactory ; with light loads, the $\alpha+\beta$ brasses are frequently found satisfactory, and the authors know of an aluminium-copper solid solution which has given remarkable results, under perfect lubrication conditions.

It appears, however, that for many purposes the structure of a

bearing metal should consist of two constituents of different hardness: the one plastic, which permits the rotating section to obtain a perfect fit or "seating," either by rapid wear of isolated sections or by general distortion or "flowing" of the plastic mass; the other hard, the object of which is to give a low coefficient of friction and to resist wear. The proportions of these two constituents will vary for different purposes.

If a bearing metal has to withstand heavy loads, it will contain a relatively large proportion of the hard constituent. If the bearing pressure is low it will contain less of this constituent. The proportions of the two constituents are obviously dependent on the chemical composition, and also on the rate of cooling (see Fig. 507, Pl. XCV., p. 243, and Fig. 508, Pl. XCVI., p. 256); the slower the rate of cooling, the more the crystals develop, and, other conditions being constant, they are less evenly distributed throughout the mass. In the lead-antimony alloys, the hard constituent is the antimony, the plastic constituent lead, or more correctly the eutectic. In the antimony-tin alloys, the Sb-Sn compound is the hard constituent.

In the ternary alloys, Pb-Sn-Bi, the bismuth constitutes the hard portion of the alloy.

The lead-tin-antimony alloys include the Sb-Sn compound in the form of clearly defined cubes together with binary and ternary eutectics.

The lead-tin-antimony-copper alloys, in which the copper is always present in small quantities (3 per cent. to 10 per cent. Cu), contain two hard constituents: SbSn and Cu_3Sn, the latter of which has already been considered under bronzes. The lead is present in the eutectics which form the plastic matrix; the SbSn occurs as regular cubic crystals; the Cu_3Sn as a meshwork of needles (Fig. 503, Pl. XCIV.; Figs. 505, 506, Pl. XCV., p. 243).

The most suitable etchants for bearing metals are:

Silver nitrate;

Dilute hydrochloric acid.

Frequently simple polishing and exposure to the air for some hours (twenty-four hours) give excellent results.

OTHER COMMERCIAL ALLOYS

Only alloys of actual practical importance will be mentioned:

Aluminium-zinc alloys, which are likely to be of greater utility in the future;

Gold-silver alloys;

Silver-copper alloys;

Gold-copper alloys; this and the previous series of alloys constituting the coinage alloys.

Aluminium-Zinc Alloys

Diagram.—*Liquidus.*—The diagram, first determined by Shepherd and subsequently revised by Rosenhain and Archbutt (1911), has a liquidus showing a eutectic point at B and a transition point C (Fig. 509).

Solidus.—The solidus consists of two inclined lines commencing from the points A and D and corresponding to the two solid solutions : α rich in zinc, and γ rich in aluminium ; also two horizontal lines passing through the eutectic point B and the transition point C respectively, and the vertical corresponding to the definite compound $\beta = Al_2Zn_3$.

Transformation Lines.—A horizontal line at 256° indicates that a transformation occurs in all alloys containing β. This horizontal corresponds to the transformation of β (Al_2Zn_3) into $\alpha + \gamma$.

Constituents.—The constituents of the aluminium-zinc alloys are :

1. An α solid solution of extremely low aluminium content (less than 1 per cent.).

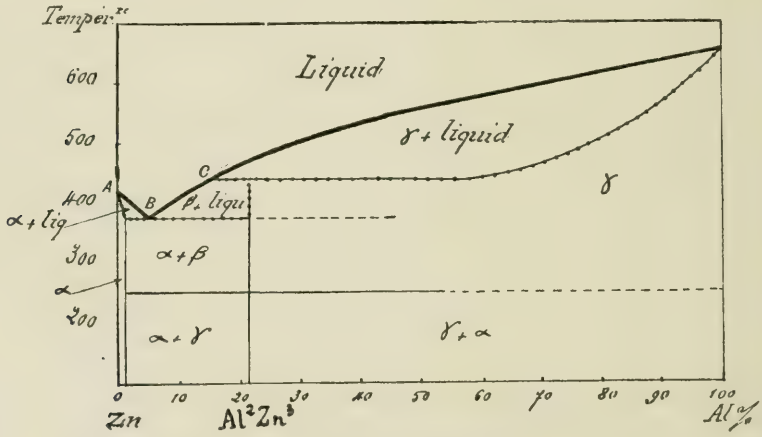


FIG. 509.—Aluminium-zinc diagram (Rosenhain and Archbutt).

2. The compound Al_2Zn_3 or β constituent which forms a eutectic with the preceding solid solution, but decomposes at 256° C. Owing to this transformation, the β constituent presents a duplex structure very similar to that of pearlite in steels, but it is only seen in alloys that have been slowly cooled.

3. The mixed crystals (Al_2Zn_3–Al) forming the γ solid solution.

Properties.—An extremely interesting industrial research has been published (see Rosenhain and Archbutt, "Tenth Report Alloys Research Committee," 1912) which shows that certain of these alloys possess very remarkable properties. Several typical examples may be quoted (rolled and annealed material).

Zinc content.	Ult. strength (tons sq. in.)	E (tons sq. in.).	Percentage elongation.	Percentage reduction in area.
5	8·8	8·5	21·0	69·9
9	10·8	10·0	21·5	61·7
13	14·2	10·3	19·7	55·7
15	16·6	13·8	22·0	50·2
20	22·1	20·1	5·5	8·3 (errors)
26	24·6	22·0	11·2	13·3

One of the authors [1] had, previous to this research, obtained the following results :—

Zinc percentage.	Treatment.	Ult. strength (tons sq. in.).	Percentage elongation.	Reduction in area.
10·2	Forged	11·5	33·5	55·4
	Forged and annealed ..	9·3	38·0	64·5
16·0	Forged	16·0	23·0	47·4
	Forged and annealed ..	14·6	28·0	41·0
21·0	Forged	19·8	14·0	27·0
	Forged and annealed ..	19·9	14·5	36·5

Several of these alloys might be compared with mild steel, but they appear to withstand repeated strains far less than steel.

Gold-Silver Alloys

Diagram.—The liquidus consists of a curve joining the melting-points of the two metals (Fig. 510). The solidus very closely approaches the liquidus. The gold-silver alloys consist of an uninterrupted series of solid solutions.

Silver-Copper Alloys

Diagram.—The liquidus consists of two curves which meet at the composition (71·9 per cent. Ag) at a temperature of 778° C. The solidus consists of a horizontal passing through this temperature and extending to the right to within 94 per cent. Ag and to the left to within 2 per cent. Ag.

At the two extremities of the diagram there are solid solutions of low contents of silver and copper respectively. These two solid solutions form a eutectic, which was for a considerable time regarded as the compound Ag_3Cu_2, until microscopical examination defined its true constitution. Actually the eutectic contains 27·9 per cent. Cu.

Copper serves to increase the hardness and tenacity of silver. The solid solution rich in copper possesses practically the same properties as pure copper.

[1] Portevin, *Rev. de Met.*, vol. viii. p. 727, 1911.

Gold-Copper Alloys

Diagram.—The liquidus and solidus each consist of a single curve, and the curves have a common minimum value (Fig. 512).

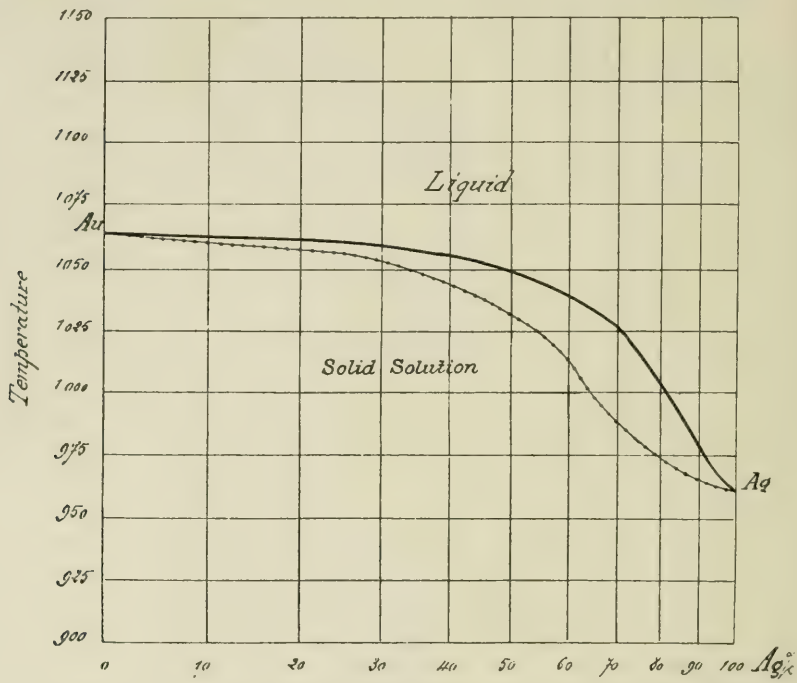


FIG. 510.—Gold-silver diagram (Roberts-Austen and Kirke Rose).

This system consequently belongs to Type III., Roozeboom (see Fig. 32, p. 34). After solidification the alloys consist of a solid

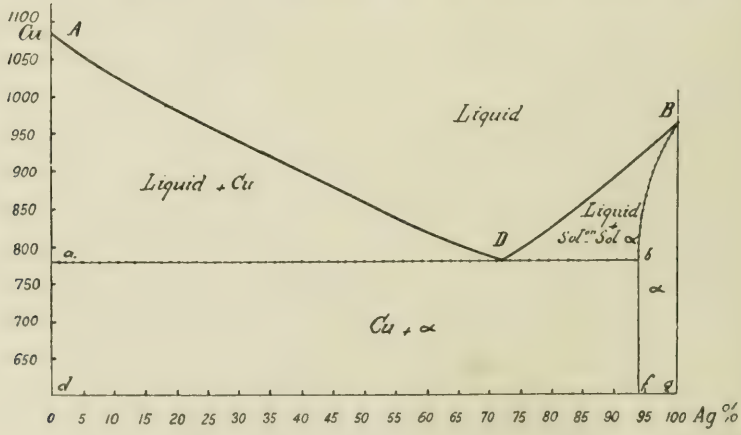


FIG. 511.—Silver-copper diagram (Friedrich and Leroux).

solution which is usually distinctly heterogeneous in cast metal (Fig. 106, Pl. XIII. *cont.*, p. 78).

In a recent research,[1] Kurnakow, Zemczuzny, and Zasedatelev have shown the existence of transformation curves with two maximums at 371° and 367°, corresponding to the definite compounds CuAu and Cu_3Au, which form solid solutions (Type II., Roozeboom, Fig. 31, p. 34). These transformations are slow and conform with

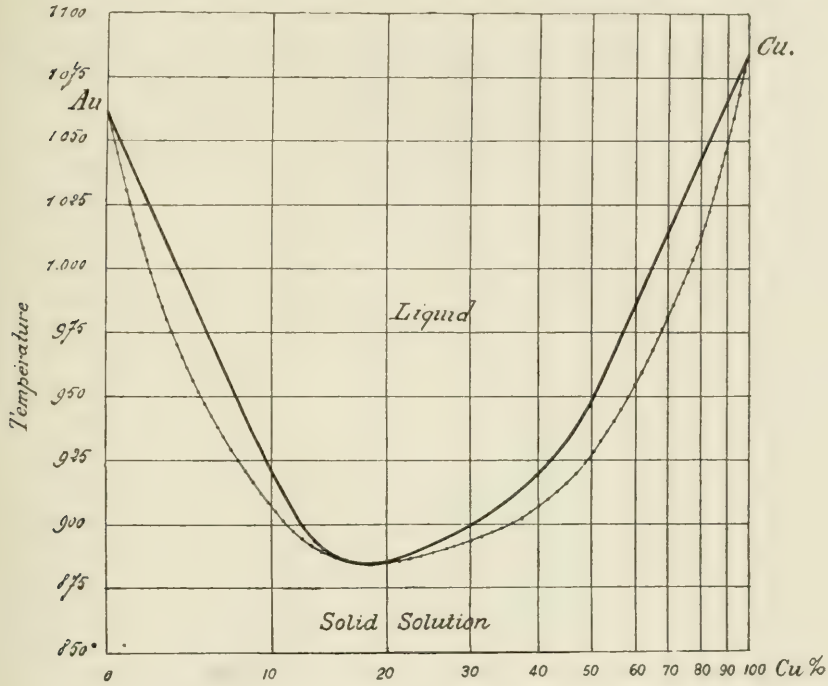


FIG. 512.—Solidification of gold-copper alloys (Kurnakow and Zemczuzny).

the general considerations given in Chap. II., pp. 73, 76. They produce Widmanstaetten structures.

The definite compounds CuAu and Cu_3Au are brittle (see Relation between Mechanical Properties and Constitution, Chap. III., p. 106), and this also applies to the solid solutions which they form. Quenching produces the primary solid solution which is malleable, and is composed of the two malleable metals gold and copper. Quenching, therefore, renders these alloys malleable and ductile, a fact which served as the starting-point for a research[2] on these alloys in 1914, and which has been interrupted by the war.

The impact figures had shown an excessive brittleness for the alloy containing 20 per cent. Cu when in the cast state and not quenched. These alloys are quenched after casting and before rolling.

[1] *Jour. Inst. of Metals*, vol. xv. p. 305, 1916.
[2] Portevin and Durand.

Lead-Arsenic Alloys

The alloys used in the manufacture of lead shot have a very low arsenic content (0·8–0·9 per cent. As).

This addition causes them to take a spherical form and a moderate hardness when cast from a great height by falling through air (shot tower).

The study of the constitution of these alloys has been made by Heike, who has constructed the diagram (Fig. 513).

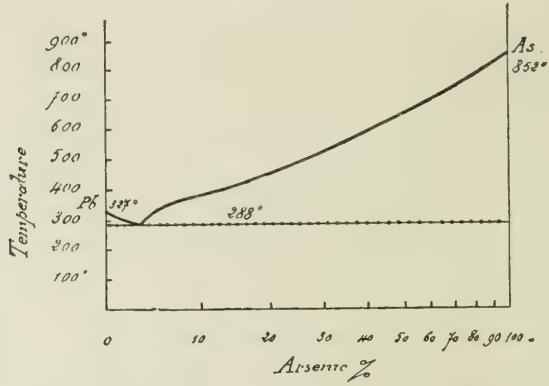


FIG. 513.—Lead-arsenic diagram (Heike).

The lead-arsenic alloys consist of two constituents, which form a eutectic that melts at 228° C., and corresponds to the composition 3·16 per cent. As.

BEARING METALS (*cont.*).

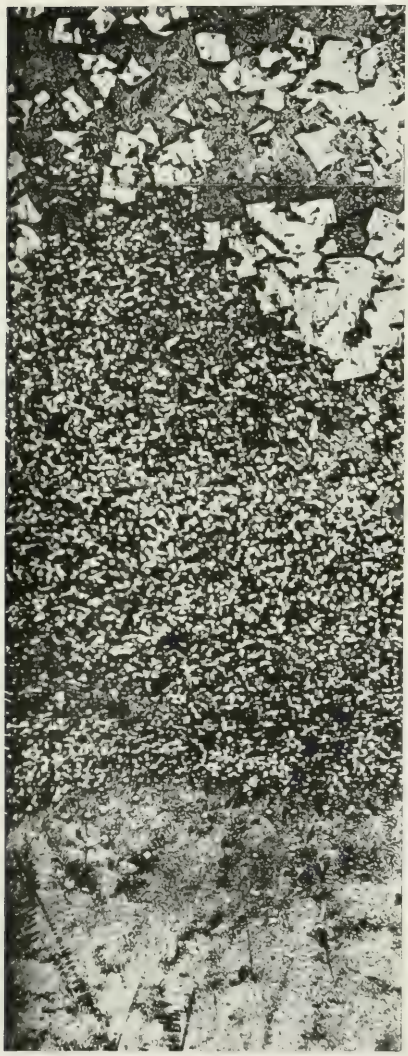
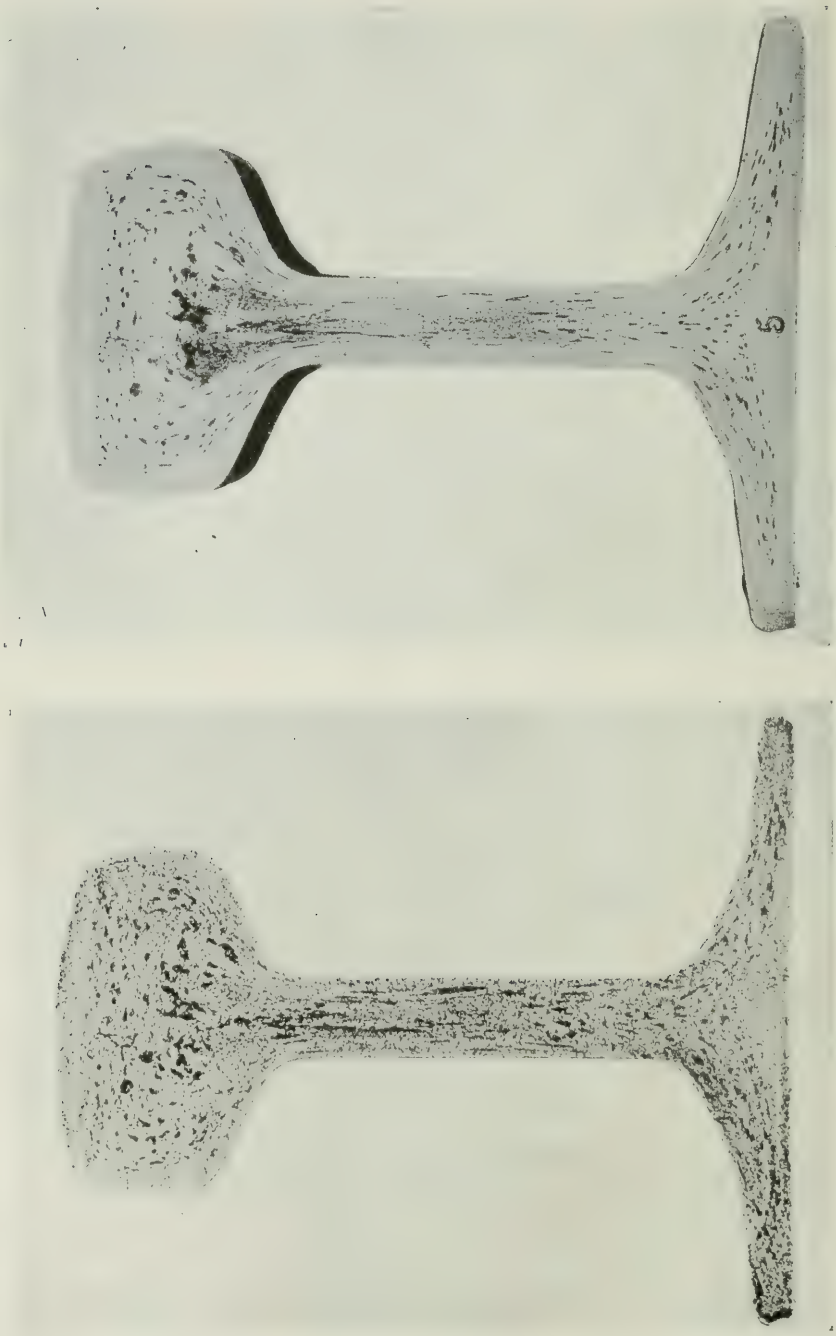


FIG. 508.—Specimen of bearing metal slowly cooled at the top and quickly cooled at the bottom.

Showing the formation and collection of the cubes at the top of the section.

ETCHING TESTS—ACTION OF REAGENTS.



Figs. 514-515.—Two macrographic etchings of the same section of steel rail. (Frémont.)

Fig. 514.—Shows deep etching with dilute sulphuric acid.

Fig. 515.—Rapid etching with a solution of iodine in potassium iodide.

PART II

MACROGRAPHY

CHAPTER VI

PRINCIPLES AND TECHNIQUE

When conclusions are drawn from microscopical, chemical, mechanical, and other investigations carried out on one or more samples or test-pieces, taken from various positions in the article or ingot considered, it is usual to assume that these conclusions are applicable throughout the whole mass of the material. This assumption, to be accurate, requires that the article shall be of uniform chemical and structural composition, and possess similar mechanical properties throughout the mass ; therefore, any systematic examination should have, as a preliminary, some method of determining whether this uniformity exists. This is provided by macrographic examination, which consists in the investigation, as a whole, of one or more complete sections, which are cut in varying directions dependent on the shape and method of manufacture of the article. The examination is made with the naked eye or, under very low magnifications, by means of a hand lens after simple polishing and suitable etching.

Again, let it be assumed that the material is of uniform chemical composition, which implies that samples taken throughout the mass give practically identical results by chemical analysis. Microscopical examination will provide the necessary information as regards the constitutional heterogeneity of any sample, as described in the previous chapters, but the microscope, of necessity, only permits small areas to be examined, the diameter of the individual field of view being usually of the order of a millimetre or even a fraction of a millimetre. Therefore, by such examination, it is difficult or even impossible to appreciate the arrangement and general distribution of the constituents, since the total area or even a portion of this area is of far greater dimensions. In such instances, macrographic examination provides the necessary information as to the general structural distribution, termed " *macrostructure* " of the alloy. Thus macrographic examination has a double application :—

1. To ascertain whether the article or ingot is of uniform chemical composition and possesses similar or varying properties throughout the mass, the homogeneity being principally dependent on the method of manufacture.

2. It is a means of estimating the general structural distribution or " macrostructure " of the material.

In the first case, such an examination is essentially an acceptance or control test (works test), but may serve also as a preliminary to a complete examination, and is then of some assistance in outlining the general procedure. The authors have reserved the term " etching-test " (essai de corrosion) for this type of examination. The object of such a test is to reveal the inequalities and defects in the homogeneity of the material.

In the second case, the test is an accurate laboratory method, the object of which is the completion of the information obtained from microscopical examination by showing the general arrangement and distribution of the microscopic particles (crystals, grains, etc.). This type of examination, made either with the naked eye or under low magnification, will be termed " *macrographic examination.*" It is not the defects that are under investigation in this instance, but the modifications resulting from the various processes to which the material has been subjected.

The perfection of the surfaces and methods of preparation are not identical in the two instances and, without encroaching on what is to follow, it may be stated that a less finished polish suffices for the " *etching test,*" whereas a polish approaching that required for microscopical examination is required for " *macrographic examination.*"

Hitherto these methods of investigation have been almost exclusively applied to steels and, although the methods to be described refer to these materials, they are also applicable, except in certain details, to all other alloys, and, as will be shown, the conclusions to be drawn from macrographic examination may be easily generalised.

The etching tests and macrographic examination will be described in this order, but such a classification is purely arbitrary and, although not very definite, it appears in practice to offer certain advantages. The principal object of the etching test is to show up the segregated areas and arrangement of the flow lines in the material, defects which may also be described as a heterogeneity of the material, and which modifications or improvements in the method of manufacture would decrease or cause to disappear.

Macroscopic examination reveals the constitutional heterogeneity which exists throughout the whole mass of the material, and is inherent in the alloy considered, corresponding to microscopical heterogeneity.

A. ETCHING TESTS [1]

Technique.—(*a*) *Polishing.*—The surface is flattened in the usual manner with a file, planing machine, or emery wheel, the finer surfacing being produced by rubbing down on emery papers of varying grades. If the complete macrographic examination is to serve as a preliminary to microscopic examination the polish must be as nearly perfect as possible, but owing to the large areas of the specimens this operation becomes exceedingly tedious. Unequal working or heating of the surface of the specimen during the flattening or rubbing-down process must be avoided, as the result of such treatment will appear on etching the specimen, the marks of the tool or abrasive then being apparent. When such effects are expected it is advisable to use fine files for the final stages of the rubbing-down process.

It is obvious that the perfection of the polish required is dependent on the nature of the examination; whether rapid works examination, detailed examination for the purpose of research, or a report on the material.

It is essential that all traces of grease, arising from the polishing operations or contact with the fingers, should be removed from the surface of the specimen; and this may be done by washing or wiping the surface with a wad of cotton-wool saturated with alcohol or, more easily, by final polishing on a sheet of clean fine emery paper—the latter method is simple and very satisfactory.

Also, it is advisable to follow Frémont's recommendation, that the operator should only rely on his own polishing and should repolish the specimen prior to etching.

(**b**) **Reagents.**—These may be divided into three main categories.

1. *Rapid etching reagents* which produce the required result in a period varying from a few seconds to several minutes, amongst which may be mentioned:

(*a*)	Pure hydrochloric acid.	
(*b*)	Iodine, sublimed	10 grms.
	Potassium iodide	20 grms.
	Water	100 c.c.
(*c*)	Heyn's reagent [2]:	
	Copper-ammonium chloride	10 grms.
	Distilled water	120 c.c.

2. *Slow etching reagents* which may require several hours or even days to produce the required effect; dilute sulphuric acid being a typical example of this class.

Sulphuric acid	20 c.cs.
Distilled water	100 c.cs.

[1] In the description of etching tests frequent extracts have been made from the paper published by Frémont, "Essais des fers et des aciers par corrosion" (*Rev. de Met.*, vol. v. p. 649, 1908).

[2] This reagent keeps indefinitely, and may be prepared and stored in bulk: the

3. *Contact reagents* by means of which a print or image is obtained on some material placed in contact with the polished face of the specimen. The contact prints on silk (Heyn and Bauer) and bromide paper (Baumann) may be cited as examples. These will be described under the heading, "Methods of Etching."

Many other etching reagents are in common use and might be mentioned, but in general it is advisable to limit their number as far as possible and thereby acquire experience in their use.

Those already described will satisfy all requirements; hydrochloric acid is a works reagent to enable rapid results to be obtained; while for more accurate or delicate work, the iodine solution as a rapid reagent and the dilute sulphuric acid as a slow reagent will be found entirely satisfactory. Finally, Heyn's reagent (copper-ammonium-chloride), which has already been mentioned as a microscopic reagent, will be found especially useful when the macrographic examination serves as a preliminary to the complete microscopic examination. The contact reagents are confined to the examination of the distribution of sulphur and phosphorus.

Methods of Etching.—With the slow etching reagents and Heyn's reagent the etching operation is performed by immersion of the specimen, but with the other rapid reagents it is usually found desirable to daub or paint the specimen with a brush containing the solution. In works practice extremely large areas are frequently examined and consequently immersion, apart from the large amount of reagent required, is liable to give unsatisfactory results owing to the grease, dirt, rust, etc., attached to the specimens, affecting the action of the reagent—considerations which are of far less importance in the case of slow etching with dilute sulphuric acid.

The detailed description of the various methods of etching will now be given.

(*a*) *Slow etching.*—The specimen is immersed in the reagent and it is sufficient to wash the specimen two or three times per day by placing it in the stream of running water from a tap, thereby removing any adherent deposit.

(*b*) *Rapid etching by painting with a brush* (Frémont).—The specimen to be etched is placed, polished face upwards and practically horizontal, in a sink; the water tap is fitted with a length of rubber tubing by which means a stream of water may be directed to any portion of the specimen in order to stop or retard the etching at any point as required; then the operation is commenced by wetting the whole surface of the specimen with water—the water should remain as a thin film over the entire surface of the specimen to ensure that

commercial copper ammonium chloride on solution usually has a white cloudy appearance, but this precipitate of copper chloride settles and may be disregarded.

the surface is free from grease and any foreign matter, and to enable the reagent to be spread evenly over the surface by means of the brush—and the painting of the *whole* surface is done as rapidly as possible to avoid unequal etching and staining. The procedure is similar to that followed in selected development or reduction of bromide prints. The etching is continued by distributing the reagent, as needed, by means of the brush, where the action ceases, and by washing with water wherever the specimen becomes covered with precipitate, in order to prevent staining.

Until experience has been obtained, it is advisable to repeat the operation, after repolishing on emery papers, and by comparison to ensure that the two images obtained are in accordance with each other; this is advisable as it is easily possible to produce staining effects which may lead to an incorrect interpretation.

(*c*) *Copper-ammonium Chloride Reagent* (Heyn).—The polished surface having been cleaned with a wad of cotton-wool impregnated with alcohol, the specimen is rapidly immersed in the reagent, polished face upwards, care being taken that the whole surface is equally covered, as otherwise stripes or bands are produced on the surface. The action of the reagent is electrolytic; it deposits spongy copper on the polished surface, an equivalent amount of iron entering into solution; it is therefore essential to avoid the presence of air bubbles, which hinder or prevent the deposition of copper, leaving small bright spots on the surface of the specimen. The reagent must be kept in continual motion, as otherwise it will vary in concentration in different parts, especially with large specimens, causing unequal etching and thereby leading to incorrect interpretations. The time required for etching is usually one to two minutes.

The copper deposit is finally removed by wiping with a wad of cotton wool in a stream of water (this operation is easily carried out if the reagent is of correct strength and the temperature has not been too low—the best temperature is between 16°–18° C.). Alcohol is then poured over the specimen until all the water has been removed, when it may be dried with a clean piece of fine linen.

The washing with alcohol is very important if rapid rusting of the specimen is to be avoided.

(*d*) *Contact Processes.*—These tests are used to reveal the sulphur and phosphorus segregation. The operation is as follows: When acted upon by acid, the sulphides and phosphides of iron decompose with the local evolution of H_2S and PH_3 which may be made to discolour a surface suitably sensitised.

In this class of reagent, that of Heyn and Bauer consists of silk impregnated with acid bichloride of mercury which reveals the sulphide areas; and that due to Baumann, of bromide paper, which

indicates the sulphide and phosphide areas. The first method, which is the more delicate, requires considerable manipulative ability ; the second, which is easily performed, is suitable for rapid methods of examination.

Heyn and Bauer's Process.—On the polished surface is placed a piece of silk which is impregnated with the following solution by means of a brush or wad of cotton wool :—

Mercury bichloride	10 grms.
Hydrochloric acid (sp. gr. : 1·124)..	20 c.c.
Distilled water	100 c.c.

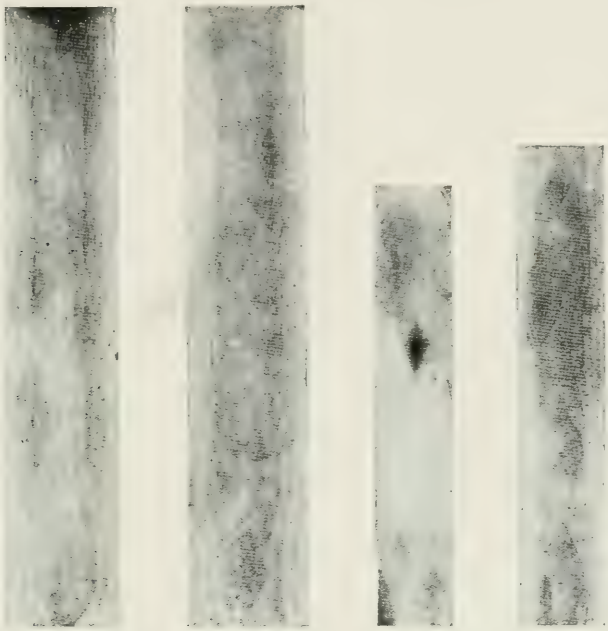
The evolution of H_2S forms a black precipitate of sulphide of mercury, adhering to the silk at the points corresponding to sulphide inclusions. As a general rule, the operation requires four or five minutes. Large evolutions of H_2S form bubbles under the surface of the thin silk, but these may be made to disappear by touching them lightly with a brush impregnated with fresh solution ; it is essential that the silk shall adhere perfectly to the specimen throughout the experiment ; also, from time to time, it is necessary to replace the used solution with fresh solution by painting over the surface with the brush. Finally, the silk is removed and carefully washed with water to remove all traces of acid without removing the black precipitate. The silk furnishes an exact image of the areas rich in sulphide inclusions, and if the sulphide inclusions are regularly distributed throughout the material, the silk will be of a uniform pale grey colour, without any marked points of contrast.

The areas rich in phosphorus evolve phosphoretted hydrogen, which forms a lemon-yellow precipitate of mercury phosphide ; therefore these are distinct from the sulphide spots, which are black. The evolution of phosphide is very slight compared to the evolution of H_2S which is extremely rapid.

Baumann's Process.—Bromide paper is wetted by immersion in dilute sulphuric acid (3 per cent.) and the sensitised surface is then brought into contact with the polished surface of the specimen to be examined, movement of the paper and the presence of air bubbles being avoided. The paper is left in contact for some definite period (20 seconds to 5 minutes), and on its removal there is found an image of varying intensity outlining the sulphide and phosphide areas by the local production of sulphide or phosphide of silver (Figs. 557, 558, Pl. CXV.). If further proof is needed, it is necessary to remove the attacked surface with a file or by other suitable means before repeating the experiment.

Choice of Etching and Photographic Record (Figs. 514, 515, Pl. XCVII.).—Rapid etching gives immediate results, but only gives a superficial image which is easily destroyed and must be covered with a protecting varnish if it is to be preserved.

LIQUATION AND SEGREGATION.



Thomas Martin Thomas Martin

1000 kg. ingots. 250 kg. ingots.

FIG. 516.—Diagrams, showing the distribution of sulphur, plotted from results obtained by chemical analysis. (WÜST & FELSER.)

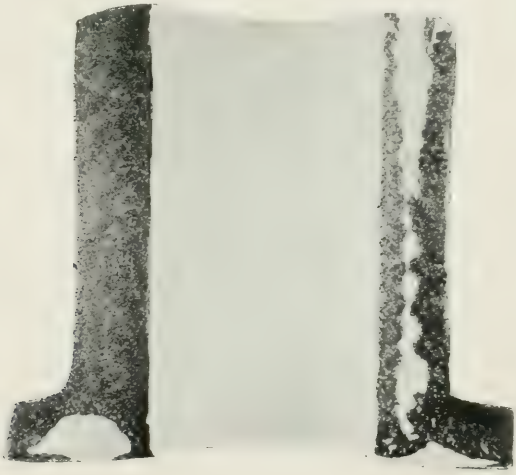


FIG. 517.—Effect of liquation.
Bronze bearing containing 30 % Pb.—The liquated lead appears white.
(× 1.)

MACROSTRUCTURE—CRYSTAL GRAINS.

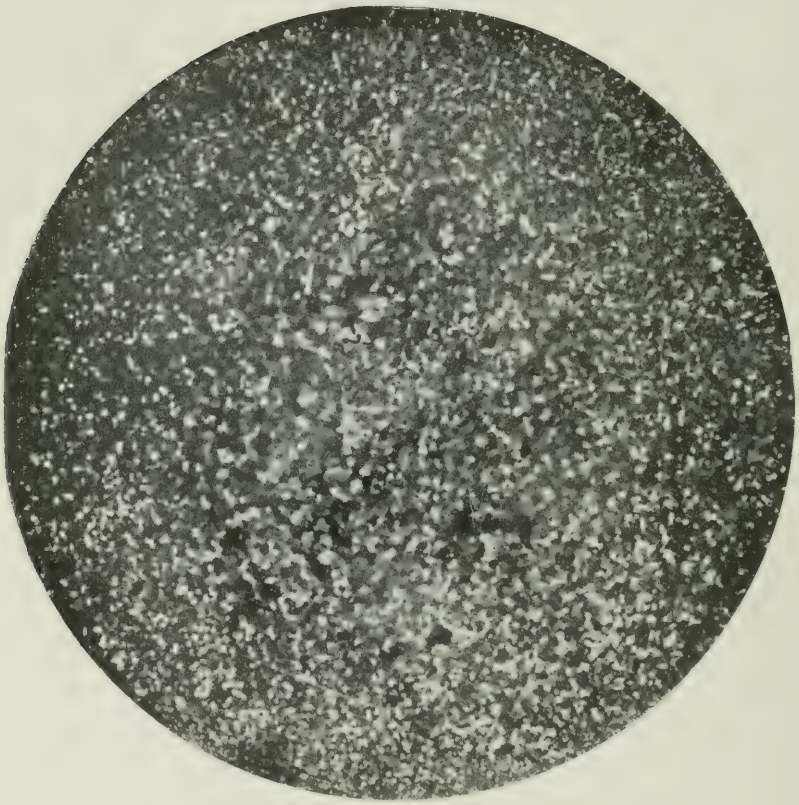


FIG. 518.—Ingot of aluminium bronze, as cast.
Etchant: Acid ferric chloride.
(× ½.)

Slow etching, on the other hand, affects the metal to a considerable depth (it is even possible, in the case of thin specimens several millimetres in thickness, to continue the etching until the portions most affected are eaten through), giving results which may be easily preserved dry, or by spreading a thin coating of grease on the specimen. By lightly rubbing the surface of the specimen with emery paper after etching, it is possible to level up the portions in relief and thereby sharpen the image. This is of great advantage when a photograph is required; the portions repolished in this manner, with suitable illumination, appearing bright, the depressions remaining dark (Fig. 514, Pl. XCVII.).

On the other hand, slow etching does not enable an immediate result to be obtained; but when a large number of samples has to be examined, it is usually found to be the more convenient method, as several specimens can be etched simultaneously in the same bath.

The superficial images formed by rapid etching (Fig. 515, Pl. XCVII.) tarnish very readily after washing and have thin yellow and green films which, although hardly visible to the naked eye, show up in a marked manner on a photograph. When dried and varnished they give flat negatives without detail or contrast, and the best result, as suggested by Frémont, is to be obtained by photographing, with a vertical camera, immediately after etching, the specimen being covered with a thin film of water.

The contact processes provide a record which is both easy to handle and easily preserved.

Deductions to be made from Macrographic Etching.—Omitting, for the moment, the contact processes which will be fully described later, it may be stated that, as a general rule, unequal etching of the surface of a specimen is a proof of heterogeneity.

If a homogeneous reagent is employed and it is kept in motion during etching, in order to avoid the unequal etching produced in a still liquid, any inequalities of etching are undoubtedly due to the heterogeneity of the metal.

Such heterogeneity may be of three different kinds: crystalline, mechanical, chemical.

1. *Crystalline Heterogeneity.*—It has been shown microscopically that the crystal grains or particles, of which all alloys or metals are composed, are differentially attacked by the reagents, the rate of etching being dependent on the orientation of the crystal in the plane of the polished surface (*e.g.* the case of alloys chemically homogeneous in the annealed state, and therefore exhibiting no effects of cold-work, etc.), and a similar phenomenon will be observed microscopically if the grains are sufficiently large to be seen with the naked eye (see Fig. 518, Pl. XCIX.; Figs. 519, 520, Pl. C.;

Fig. 524, Pl. CII.). With ferrous alloys this condition will only be found in cast metal or burnt steels; the most suitable reagents are nitric acid and Heyn's reagent. As this subject concerns other alloys, it will be further considered under the heading of macro-structure. Generally, with all mechanically worked steels, rolled or forged, the grains are too small to be visible to the naked eye, and therefore the crystalline heterogeneity is not visible.

2. *Mechanical Heterogeneity.*—It has been shown that an alloy of definite chemical composition is more readily attacked when in a strained (work hardened) condition; therefore, if there has been any irregular or local hardening this will be detected by variations in the etching. As this effect is only present in material that has been cold-worked or permanently deformed at low temperatures, heterogeneity due to work hardness may therefore be disregarded in the case of material that has been cast and annealed, and also, as a general rule, forged material. In a similar manner, the porous sections of the material and the welding lines are more readily attacked.

Inclusions might also be considered under the heading of mechanical heterogeneity, but it appears more desirable to deal with them under the heading chemical heterogeneity, which is the most important factor in the etching test.

3. *Chemical Heterogeneity.*—This is of the greatest importance, since it is the most frequent cause of unequal etching. The rate of etching is, of necessity, dependent on the chemical composition at any given point. In steels, the most impure portions are the first to be attacked, and the inclusions (sulphides, oxides, silicates, slag) constitute the centres of rapid etching; either, because the reagent attacks them more readily than the remainder of the material, or because, being less readily attacked than the metal, they set up an electrolytic action which brings about the corrosion of the surrounding metal.

Owing to these causes, the impure areas, the porous sections, and the portions of the material containing inclusions constitute the areas most readily attacked by etching reagents.

The origin of chemical heterogeneity must now be considered:—

1. It may be intentional (cementation) or due to the method of manufacture (welding, cemented steel, etc.).

2. It may be due to the phenomena of liquation and segregation accompanying solidification; the effects of which phenomena may be restricted or localised by special precautions, but which are always present in some degree and will now be briefly considered.

Phenomena occurring during the Solidification of Alloys: Contraction, Liquation, Segregation.—The solidification of an alloy is accompanied by two distinct phenomena:—

MACROSTRUCTURE—CRYSTAL GRAINS (*cont.*).

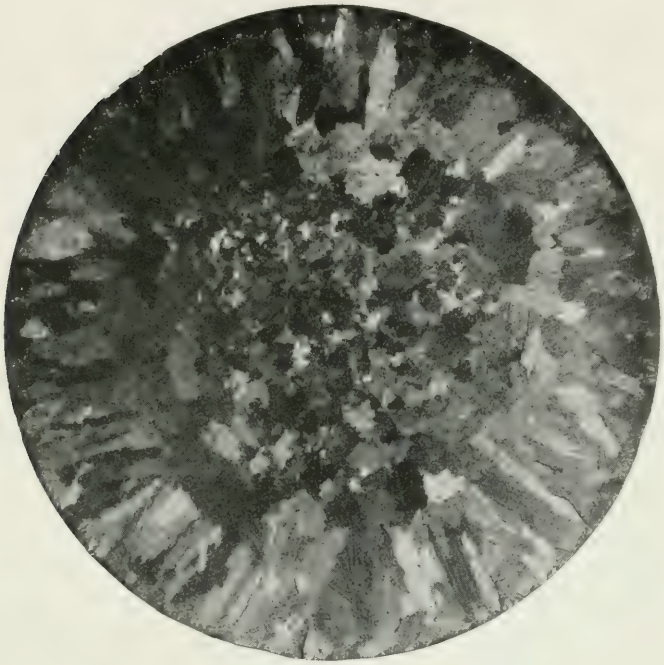
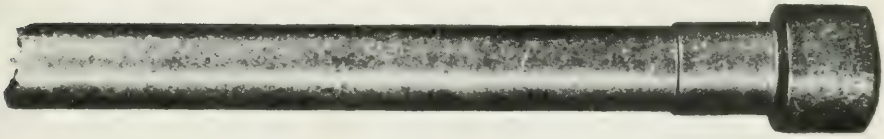


FIG. 519.—Sand cast zinc bar; as cast.
Etchant: Acid ferric chloride. Surface stains removed by gentle rubbing.



Chill cast.

Sand cast.

FIGS. 520-521.—Tensile test pieces of an alloy of the following composition:
Cu = 82·4 %; Ni = 15·0 %; Al = 2·1 %.
Etchant: Boiling ammon. persulphate solution.

MACROSTRUCTURE.—DENDRITES AND CRYSTALS.

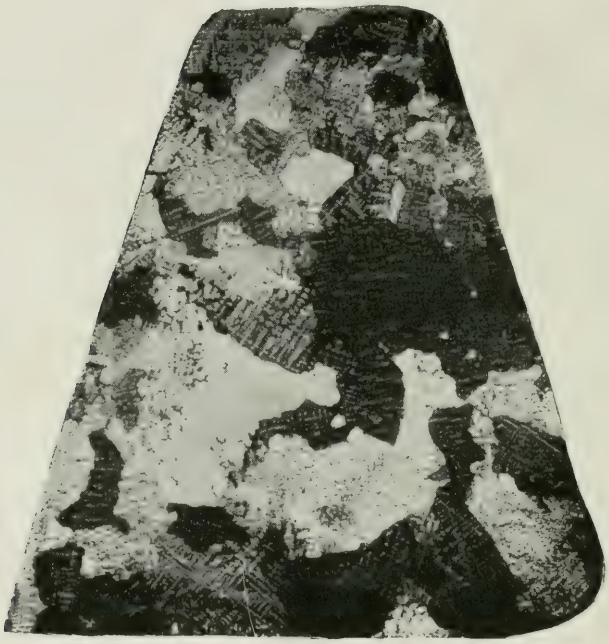


FIG. 522.—Slowly cooled cupro-nickel; 80 % Cu.
Showing dendrites and crystals.

Etchant: Copper ammonium chloride.
(× 2.)

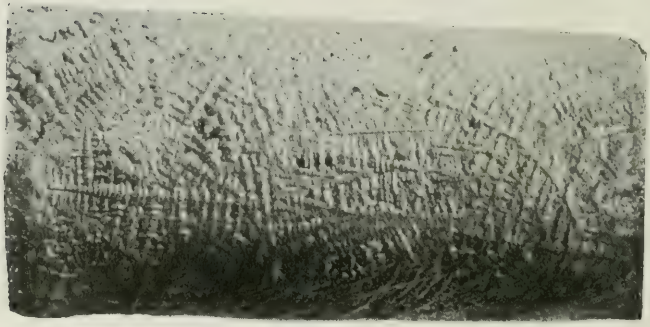


FIG. 523.—Very slowly cooled bronze; Cu = 84 %.
Showing dendrites standing out in relief.

MACROSTRUCTURE—DENDRITES AND CRYSTALS (*cont.*).

FIG. 524.—Sand cast brass ingot; as cast.
($\times \frac{1}{3}$.)

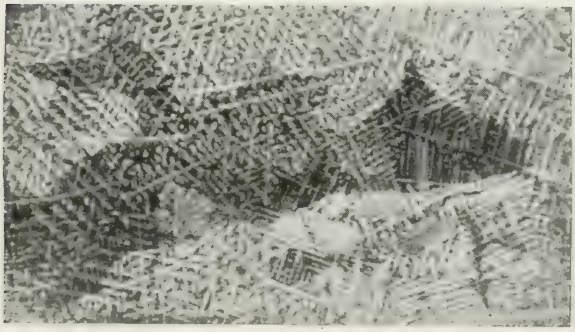


FIG. 525.—Alloy containing Cu = 82·8 %: Ni = 12 %; Al = 5 %.
As cast.

Etchant: Acid ferric chloride.
Oblique illumination.
($\times$ 6.)

MACROSTRUCTURE—DENDRITES.

FIG. 526.—Alloy: Cu = 59·7 %; Ni = 36·5 %; Al = 3·0 %.
As cast.
Etchant: Acid ferric chloride.
(× 6.)

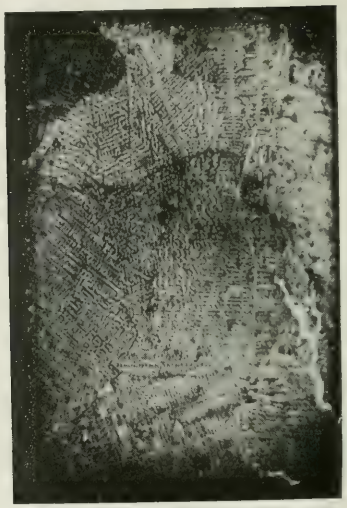


FIG. 527.—Alloy: Cu = 59·7 %; Ni = 36·5 %
Al = 3·0 %.
Annealed at 800° C.
Etchant: Acid ferric chloride.
(× 6.)

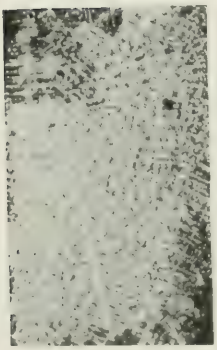


FIG. 528.—Alloy: Cu = 59·7 %; Ni = 35·0 %; Al = 5·0 %.
As cast.
Etchant: Acid ferric chloride.
(× 4.)

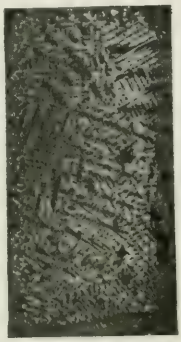


FIG. 529.—Alloy: Cu = 79·4 %; Ni = 20 %.
Annealed at 750° C.
Etchant: Acid ferric chloride.
(× 4.)

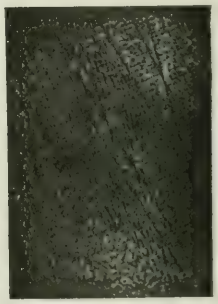


FIG. 530.—Alloy: Cu = 79·4 %; Ni = 20 %.
As cast.
Etchant: Acid ferric chloride.
(× 4.)

1. A physical phenomenon, *contraction*, causing *piping*.

2. A chemical phenomenon, *liquation*, causing the chemical *segregation* of the constituents.

The change from the liquid to the solid state is usually accompanied by a decrease in volume. In an ingot, cooling commences from the periphery in contact with the cold walls of the ingot mould, and at any given moment all the points of equal temperature are to be found on an isothermal surface, solidification continuing in successive layers. Finally, owing to the contraction on cooling, a space or pipe is produced in the upper central section of the ingot, this pipe conforming to the last solidified portions of the ingot.

But it has been shown that the solidification of an alloy, instead of occurring at any definite temperature, occurs over a given and often comparatively wide range of temperature, and that the composition of the solid phase differs from that of the liquid phase. In the case of the deposition of a solid solution, as in steels, this difference is lessened by slow and incomplete diffusion. Again, as previously stated, the cooling of an ingot occurs from the periphery inwards, leaving the residual liquid in the interior ; thus, in the case of steel, owing to carbon and the other elements (Mn, S, P) lowering the melting point, the composition of the liquid phase will be found to be higher in these elements than the solid phase. The direct result is an enrichment in carbon and the various impurities in the last portions of the metal to solidify. This enrichment is termed *segregation*, and the impurities which are found, as previously stated, in the regions round the bottom and sides of the pipe.

In practice the segregation is incorrectly termed the pipe, thereby giving the name of the cavity to the material surrounding that cavity.

The resulting ingot will be of heterogeneous composition, the final distribution of the constituents being dependent on : the temperature and the rate of casting, the nature of the metal, the viscosity of the liquid, the form of the ingot mould, the amount of agitation or movement produced by the liberation of gas, the shape and distribution of the isothermal surfaces relative to the outside of the ingot, and also on certain special processes introduced with the object of decreasing the piping—compression method (Harmet), local heating (Hadfield, Rimer, the Gutehoffnungshutte, etc.).

The distribution of any given element, manganese, for example, will be defined by the outline of the points possessing the same manganese content, termed by Osmond [1] the isochemical surfaces.

By cutting through these surfaces along one of the diametrical planes of the ingot, and analysing surface samples from all positions, it is possible to obtain a series of isochemical curves on the surface

[1] *Introduction à la connaissance des métaux ;* Com. des méthodes d'essai, 1894.

of the section of the ingot. Wüst and Felser[1] have traced the distribution curves for C, Mn, S, and P, in Marten and Thomas steel ingots (1000 to 250 kilogrammes) in this manner (Fig. 516, Pl. XCVIII., p. 262). Silicon, however, shows no tendency to liquate. It must also be noted that in any given instance the distribution of the isochemical surfaces is dependent on the distribution and displacement of the isothermal lines as well as the segregation and rate of diffusion of the various elements; and these surfaces are transformed by rolling into similar surfaces, which give varying isochemical curves in different sections.

Neglecting for the moment inclusions, porosity, and other causes of local attack or etching, it is possible to consider that the macrographic images, or curves of similar etching qualities, correspond approximately with the isochemical curves (this is not absolutely correct, as the isochemical curves for phosphorus are not necessarily the same for manganese, etc.).

It is to be observed that the deformation of the isochemical curves due to rolling does not correspond with the exterior deformation of the ingot. This is no doubt to be explained by the relatively lower malleability of the segregated portion of the ingot, for the initial square section of the original ingot will often be found in the macrographic etching of sections of round bars (Fig. 540, Pl. CVII. [p. 272]; Fig. 558, Pl. CXV., p. 274). This effect persists even in fine wire.

Deductions.—From the chemical standpoint, the etching test reveals the segregations in cast or forged metal, in other words, the impure portions of the material, and outlines the distribution of these impurities. It should therefore serve as a preliminary to all complete examinations of any material, and afford considerable assistance in the selection of representative samples for chemical, mechanical, or other examinations.

With wrought irons and welding irons, the etching test gives a banded image, and this fact enables information to be obtained as to:

1. The conditions governing systematic deformation.
2. The forging and welding processes to which any given article has been subjected.

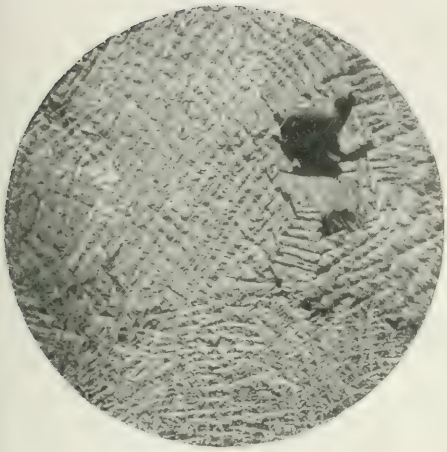
Chapter VI. deals with typical examples of this type of test.

B. MACROSTRUCTURE

General Outline.—It has been shown that the structure of metals and alloys is formed during solidification. This solidification structure or primary structure is afterwards modified or destroyed,

[1] Influence de la ségrégation sur la resistance des aciers: Congres de Metallurgie de Dusseldorf, 1910.

MACROSTRUCTURE—DENDRITES (*cont.*).



(C = 1·15 %; Cr = 7·0 %.)

FIG. 531.—Dendrites appearing in relief on the surface of a steel ingot which has been slowly cooled under a layer of slag. (N. J. BELAÏEW.) (× 1.)

(Cu = 80; Ni = 20.)

FIG. 532.—Dendrites appearing in relief on the surface of a small cupro-nickel ingot. (× 1.)

FIG. 533.—Macrostructure of a dendritic crystal obtained from the inside of the pipe of a steel ingot. (N. J. BELAÏEW.) (× $\frac{3}{2}$.)

MACROSTRUCTURE OF STEELS.

(N. J. Belaïew.)

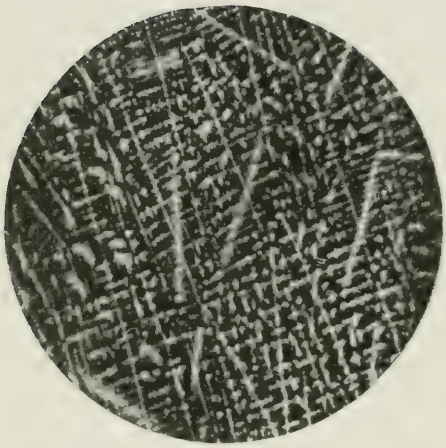


Fig. 534.—0·45 % C. steel.
Quenched from 850° C. and reheated to 550° C.
(× 5.)

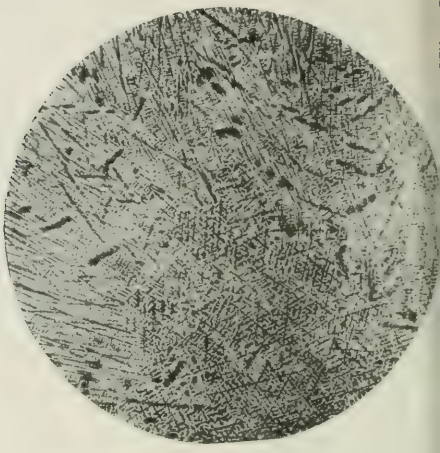


Fig. 535.—1·04 % C. steel.
Chill cast.
(× 5.)

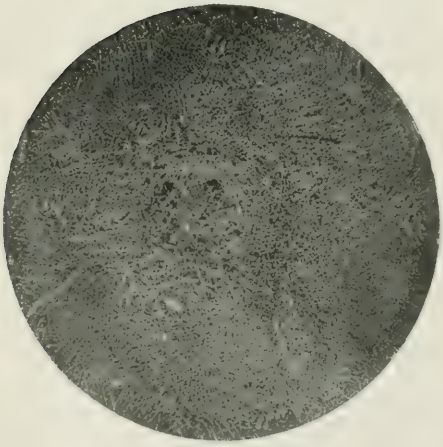


Fig. 536.—Transverse section.

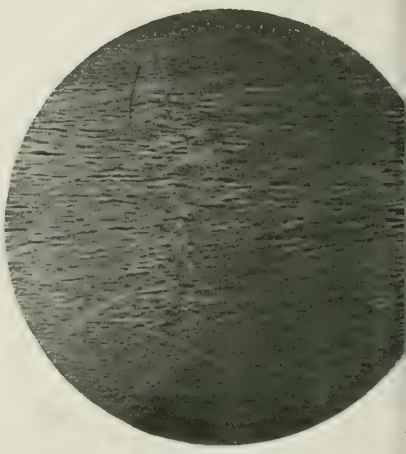


Fig. 537.—Longitudinal section.

Figs. 536–537.—0·69 % C. steel, hammered out.
Etchant: 2 % picric acid in alcohol for 30 minutes.
(× $\frac{3}{2}$.)

during the transformations which occur in the solid alloy, by heat treatment and also by mechanical treatment to which the alloy may be subjected. Frequently this primary structure has a limiting or directing chemical or crystallographic influence on the modifications that may occur later, thus producing a form of hereditary effect on the structure; it is therefore important to know and recognise such structures. It has also been shown that the size of the particles constituting the structure is dependent, other conditions being constant, on the speed of the transformation at their formation; and, more especially, that the particles of primary solidification may under certain conditions be sufficiently large to be visible to the naked eye. This latter condition arises with steels and other commercial alloys where the ingots are of sufficient size and the rate of cooling is not too great. Microscopical examination will then determine all changes of structure due to transformations and secondary recrystallisation, but will not reveal the original outlines of the primary structure. In such cases it is advisable to make a more general examination in which a greater area is embraced in order to judge the structure as a whole, since certain mechanical properties are frequently dependent on this general structure. Thus, it is obvious that the exclusive use of the microscope and photographs obtained by that means only enables detailed information to be gained and will not offer information on the general structure and those properties dependent on that structure.

The logical method of investigation is for the macroscopic examination to precede the microscopic examination of any specimen. In other words, the specimen should be carefully examined with the naked eye before interposing a magnifying apparatus between it and the eye.

The above statement leads directly to a brief review of the macrostructure of alloys of uniform chemical composition, chemical heterogeneity or segregation having been considered under etching tests. Alloys in the cast state will be considered since, except in special cases, it is the primary structure due to solidification that appears as the macrostructure. Subsequently a brief account will be given of the modifications occurring in steels due to heat and mechanical treatment.

Ingots in the Cast Condition.—It has been shown that during the formation of solid solutions—which embraces most commercial alloys, as steels, brasses, bronzes, aluminium bronzes, nickel silvers, etc.—dendrites are formed, the mutual limitations of which constitute the crystal grains; and further, that the material is heterogeneous owing to the slow rate of diffusion in the solid state, the original axes of the dendrites solidifying first being of different composition to the outer layers solidifying later. Therefore it is

possible to reveal, either the dendritic structure, which appears owing to the chemical heterogeneity, or the crystal grain structure, on the surface of a section of an ingot or other cast material by means of any suitable reagent.

Apart from work on steels, very little work has been published on the macrostructure of alloys. The authors have therefore included several photographs from an unpublished paper on the macrostructure of copper alloys. Fig. 518, Pl. XCIX. shows a section, on a reduced scale, of a sand-cast aluminium bronze, in which the crystal grains are clearly visible. Such grains are even larger in Fig. 524, Pl. CII., which illustrates a brass casting from a sand mould with four branches ; the elongation and orientation of the grains at the periphery will be observed. This effect is shown much more clearly in chill castings. Fig. 519, Pl. C., is a photograph of commercial zinc, and Figs. 64, 65, Pl. V., illustrate the difference between sand and chill casting in the case of a brass containing 58 per cent. Cu, while a similar effect is shown in Figs. 520, 521, Pl. C.

In all these instances, it is the outline of the grains that is visible owing to the varying reflecting power and coloration of the grains. The dendritic structure easily visible in the grains is not well defined in the photograph, Fig. 519, Pl. C., but the dendrites and the grain outline may be seen in Fig. 522, Pl. CI. (cupro-nickel slowly cooled). In other cases the dendrites are visible. Figs. 525–530, Pls. CII., CIII., show a series of cupro-nickel-aluminium alloys at low magnifications ($\times 4$–$\times 6$), and the dendritic outlines appear either light or dark (the inversion occurs on passing from oblique to vertical illumination).

These dendrites are also visible on the exposed surface (top) of ingots, especially when this surface is protected by some suitable molten cover (slag in the case of steel) ; for, owing to the contraction occurring during cooling, the dendritic axes, which are the first to solidify, appear on the surface in relief forming tree-like structures. Examples are shown, in the case of copper alloys : Fig. 523, Pl. CI. (bronze), Fig. 532, Pl. CIV. (cupro-nickel), slowly cooled ; and in the case of steel : Fig. 531, Pl. CIV., illustrating a chrome steel ingot, the original of which is due to the work of N. J. Bélaïew, while several of the later illustrations are from the same source. The "steel crystals" found in pipes separate in a similar manner, that described by Tschernoff being the best known example (Fig. 63, Pl. V., p. 72), and this leads directly to the more detailed examination of the macrostructure of steels. Research of this nature has recently been carried out in Russia by Captain N. T. Bélaïew, Engineer N. J. Bélaïew, and Biélinsky. In the following description the authors have attempted to combine their own researches with the above although the two are not in complete agreement.

MACROSTRUCTURE OF CAST STEEL

To reveal the structure the polish must be sufficiently perfect to ensure that no scratches are visible to the naked eye or at low magnifications. Etching may be carried out with the usual reagents, but the following reagents are recommended :

1. Two per cent. solution of picric acid in methyl alcohol ; the etching to occupy several hours (N. J. Bélaïew).

2. One per cent. aqueous solution of neutral copper-sulphate (Biélinsky). The examination is made after the deposition of the copper caused by the etching (dendritic structure) ; again after removing the deposit by washing (reticular and dendritic structure) ; and a final examination after slight rubbing down on fine emery paper (granular and reticular structure).

The results obtained with these two reagents will be considered later. The first reveals the structure, which N. J. Bélaïew terms macrostructure, and N. T. Bélaïew terms "large crystal structure," which is merely the dendritic structure due to primary solidification, and is revealed owing to the chemical heterogeneity of the solid solution formed during solidification. This may also be described as the varying concentration of the constituents of the solid solution in the first and last portions to solidify, the axes of the dendrites constituting the lines of minimum concentration (Fig. 533, Pl. CIV., Figs. 534–537, Pl. CV.).

The term "large crystal structure" results from the crystals found in pipes, which have already been described, and from the outward form of such crystals as shown by Fig. 533, Pl. CIV. In the interior of an ingot this connection is shown by the areas corresponding to faces, fractures, or sections revealed by etching. The visibility of this macrostructure is dependent on the rate of solidification, which varies more especially from the periphery to the centre of the ingot. The size of the dendrites varies inversely to the carbon content.

3. *Stead—Le Chatelier Cuprous Reagent.*—This reagent, the composition of which is given below, deserves special mention. First suggested by Stead for revealing the phosphide areas in steels, it has been further used by H. Le Chatelier and Lemoine, who, after showing that it also reveals the unequal distribution of manganese in the steel, have defined the conditions of use and preparation of this reagent, and have suggested the following formula :—

Pure methyl alcohol	100 c.c.
Water	18 c.c.
Hydrochloric acid, conc.	2 c.c.
$CuCl_2,2H_2O$	1 grm.
$MgCl_2,6H_2O$	4 grms.

Ethyl alcohol may also be used, according to the following formula suggested by H. Le Chatelier :—

Ethyl alcohol, 95°	100 c.c.
Water	10 c.c.
Hydrochloric acid, conc.	2 c.c.
$CuCl_2,2H_2O$	1 grm.
Picric acid	0·5 grm.

The relative proportions of alcohol and water must be accurate if a good result is to be obtained. The etching is performed by wetting the polished surface with the reagent, observing the progress of etching, and stopping the reaction when required by washing the specimen.

In practice the action of this reagent appears to be affected by all the elements in solid solution in the steel, and it is therefore an extremely suitable reagent for revealing the primary macrostructure due to the dendritic structure of primary solidification. With polished surfaces of large area the following method of operation will be found convenient : the surface is completely covered with copper by immersion in the reagent, after which the macrostructure is revealed by gentle rubbing with a cloth impregnated with paste or metal polish. The sections shown in Figs. 559, 560, Pl. CXVI. (p. 274), have been prepared in this manner.

Effect of Heat Treatment.—The usual heat treatments—annealing, quenching, tempering—do not affect the macrostructure, for the original structure showing the unequal concentration of the original solid solution persists, owing to the negligible effects produced by diffusion. The macrostructure, however, shown by etching with picric acid shows up particularly clearly after quenching at 900° C. in water and tempering to 650° C., as already described by Osmond.

Effect of Mechanical Treatment.—On the other hand, mechanical treatment at high temperatures, such as forging, rolling, etc., completely deforms the macrostructure and brings about the alignment of the dendritic outlines in the direction of elongation of the metal. This fact is shown in Figs. 536, 537, Pl. CV., which illustrate transverse and longitudinal sections of a forged bar, 5 centimetres in diameter, obtained from a 10 cm. × 10 cm. ingot, in which the "fibres" of the original metal are clearly visible. These are the "flow lines" that Cloup [1] has mentioned in connection with forged and stamped steel. Contrary to the usually accepted statement, rolling or forging does not "produce" or "create" these lines ; they already exist before such operations, but are entangled and have no definite parallel orientation—this general direction is given to them by the above treatment (Fig. 547, Pl. CX., p. 272 ; Figs. 559, 560, Pl. CXVI. ; Figs. 561, 562, Pl. CXVII., p. 274).

[1] *Rev. de Met.*, vol. vii. p. 605, 1910.

It is probable that the variations in the mechanical properties of cast and rolled steels of the same chemical composition and the same microscopic structure are related more especially to the variations in macrostructure, and, as already mentioned, these differences will persist after the heat treatment to which the metal may be subjected.

The macroscopic outline combined with the effects produced by inclusions explain the difference in properties of steel obtained from samples taken longitudinally and transversely to the direction of forging.

Secondary Structure.—It has been shown that the chemical heterogeneity of the solid solution produced by primary solidification tends to the formation of a dendritic structure. A brief description must now be given of the subsequent transformations, viz. separation of the pro-eutectoid constituents and the formation of pearlite. The pro-eutectoid constituents, ferrite and cementite, separate along the edges of the grains of the iron-carbon solid solution, forming a network, in addition to which the separation may be completed in the interior of these grains (Widmanstaetten structure) ; it is this that constitutes the Biélinsky " reticular structure," [1] which appears after removing the copper deposit produced by his reagent.

If, after the above operation, the surface is rubbed with fine emery paper (000), the " granular structure " (French " structure grenue ") appears, and consists of small reflecting surfaces, the brightness of which varies with the direction of illumination. This is, in the authors' opinion, the actual crystalline structure of the steel, and corresponds to the α iron and the pearlite grains. It is directly related to the structure obtained on fracturing steel at ordinary temperature.

Such structures will obviously be visible macrographically if the conditions during their formation are such as to enable them to become sufficiently developed.

Biélinsky [1] has examined the relations between these various structures.

Conclusions.—The stability of the macrostructure after heat treatment shows that it is dependent on the solidification conditions and illustrates the " hereditary " effect of this operation on the properties of the steel. The changes produced in the macrostructure by mechanical treatment at high temperature afford some explanation of the resulting effect produced on the mechanical properties. Finally, the examination of the macrostructure after such treatment provides valuable information as to the effects produced and, inversely, may offer considerable assistance in the choice of the most suitable treatment.

[1] *Rev. de Société russe de Mét.*, pp. 396–426, 1912.

CHAPTER VII

THE INDUSTRIAL APPLICATIONS OF MACROGRAPHIC EXAMINATION

MACROGRAPHIC examination may constitute a separate examination or may be used as a preliminary to a chemical or mechanical examination of any material. In the case of steel, it reveals segregation and local defects; with welded articles, it shows up the welding lines and the varying composition of the material surrounding the weld or the welding material; with wrought iron or welding iron, it serves to indicate the method of forging and indirectly constitutes a method of examining the sequence of operations for any systematic deformation. The macrostructure shows the method of forging equally well in the case of homogeneous steel.

Examples are given of various typical instances; several of these examples have been obtained from Frémont's paper on this subject.

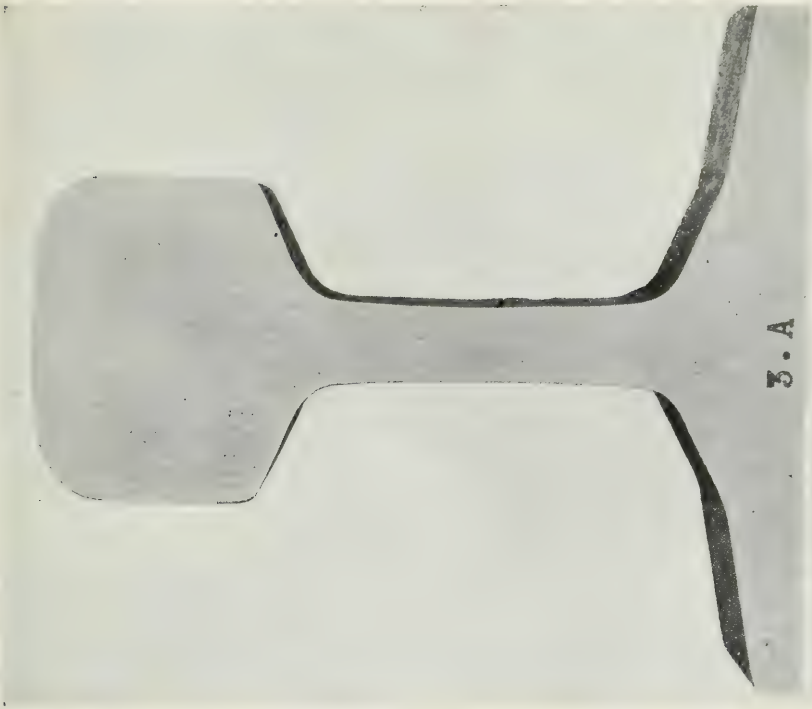
1. **Examination of Segregation.**—It has been shown (p. 263) that the etching tests and contact processes (sulphur prints) reveal the impure sections and inclusions in the material which result from the chemical inequality due to liquation. In this manner differences in steel rail sections formed from the top and bottom portions of an ingot are clearly revealed (Figs. 538, 539, Pl. CVI.).

To reduce, or eliminate, the amount of segregation, the amount of reject from the ingot ("crop") is increased; but it must be noted that the shape and size of the pipe is governed by many factors such as, the purity of the metal, the shape of the mould, the method of casting, and also by various operations connected with the local heating or cooling of the ingot during casting, and even by mechanical methods such as compression (Harmet process).

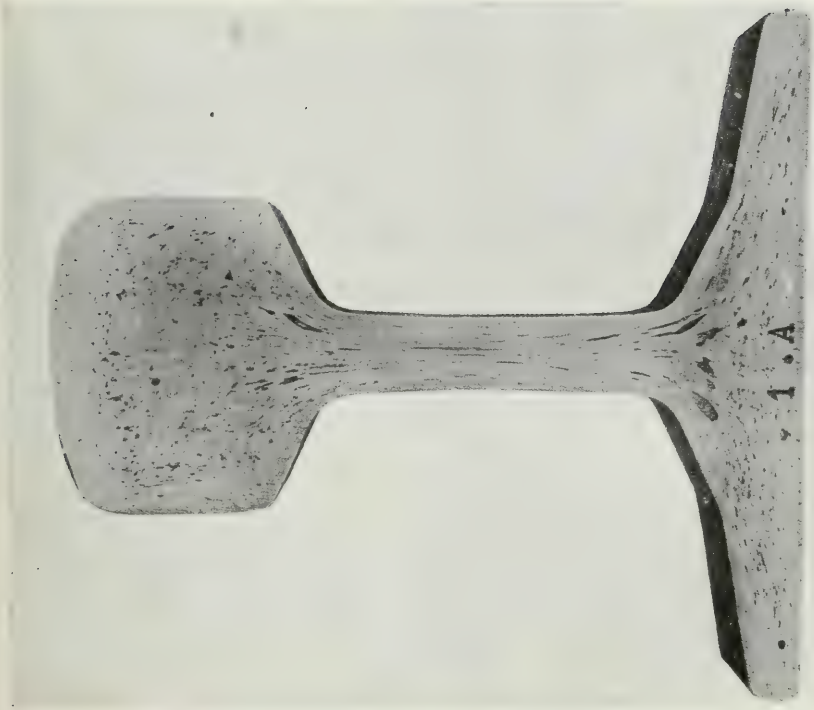
Moreover, the presence of constituents from the segregated portion of an ingot may not only lower the average quality of the metal, but may also lead to the formation of faults and surface cracks in the material which slowly increase in size and importance and, after continual service, eventually extend to the other sections of the material, causing sudden fractures during use (Fig. 540, Pl. CVII., and Fig. 542, Pl. CVIII.).

Several serious accidents caused by the fracture of steel plate

ETCHING TESTS—SEGREGATION EFFECTS.



Bottom of ingot.



Top of ingot.

FIGS. 538–539.—Etching tests on a steel rail. (FRÉMONT.)

ETCHING TESTS—SEGREGATION EFFECTS (*cont.*).

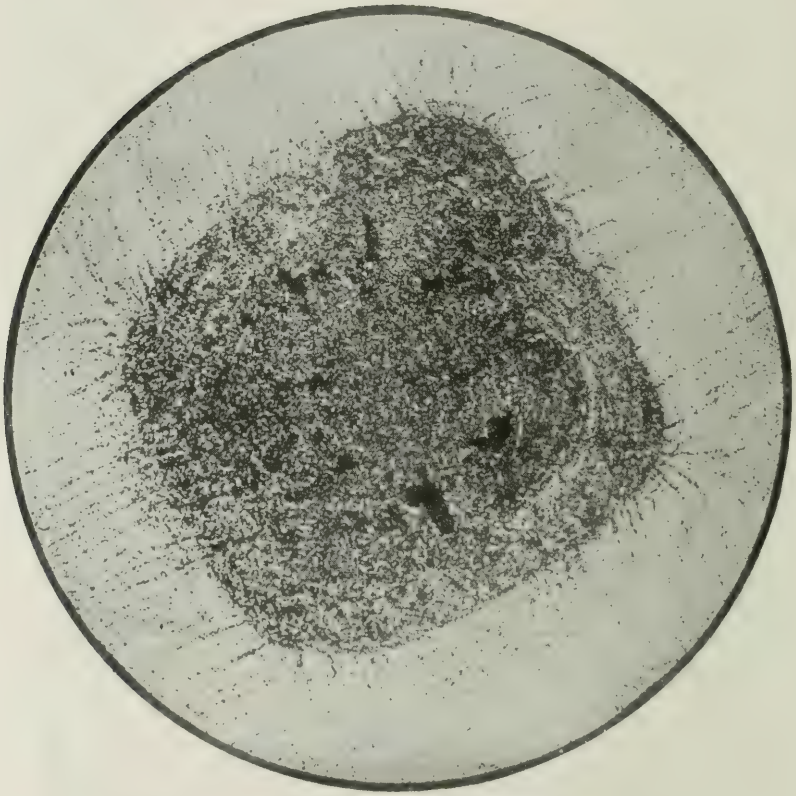


FIG. 540.—Section of steel bar fractured in use. (FRÉMONT.)
Slow etching.

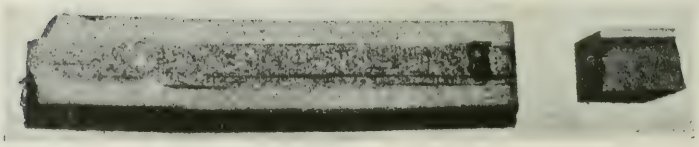
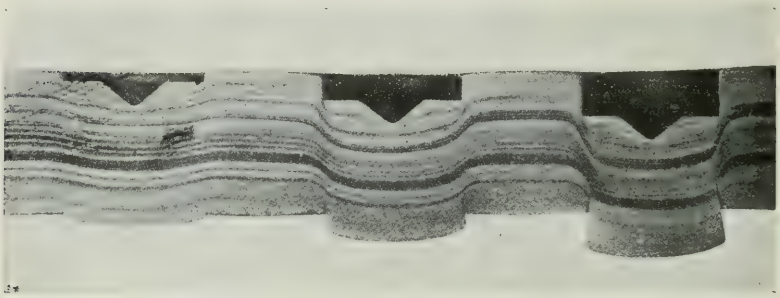


FIG. 541.— Sheet steel fractured in use. (FRÉMONT.)

ETCHING TESTS—EFFECTS DUE TO INCLUSIONS.

FIG. 542.—Section of an automobile axle-arm which has fractured in use, showing the lines of inclusions and the accumulation of these inclusions near the fracture. Etching: Slow etching followed by slight repolishing.

ETCHING TESTS—EFFECT OF MECHANICAL DEFORMATION AND THE METHOD OF MANUFACTURE.



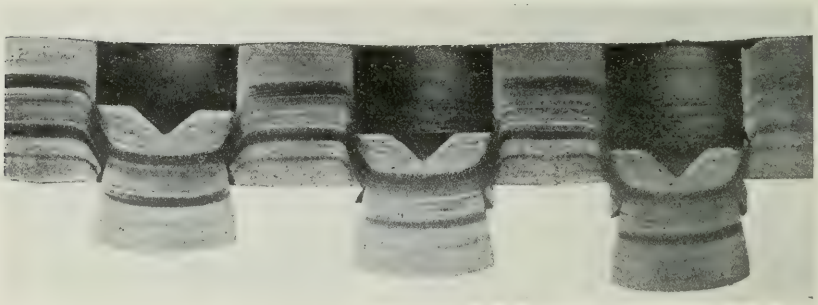


FIG. 543.—Illustrations of mechanical deformation.
Successive stages in the stamping of a puddled iron bar. (FRÉMONT.)
Rapid etching in concentrated hydrochloric acid.

FIGS. 544-545.—Influence of the method of manufacture on the arrangement of the flow-lines of the metal.
Rivets flattened hot. (FRÉMONT.)

FIG. 544.—Hand hammered.

FIG. 545.—Machine hammered.

ETCHING TESTS—INFLUENCE OF THE METHOD OF MANUFACTURE.

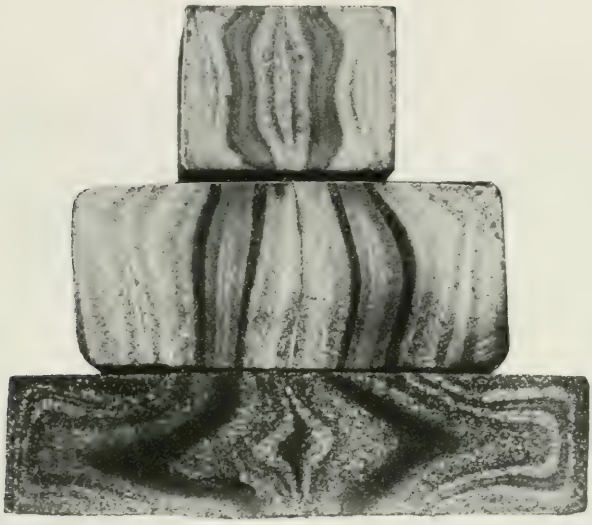


FIG. 546.—Various sections of steel which have been welded and then pressed flat to determine the quality of the welds.
Etchant: Prolonged etching with Bénédicks' reagent.

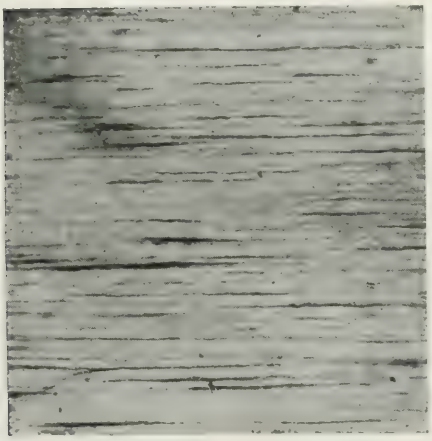


FIG. 547.—Silico-manganese steel.
Longitudinal section.
Etchant: Bénédicks' reagent.—Oblique illumination.
(× 5.)

FIG. 548.—Forged section with welded inset.

ETCHING TESTS—INFLUENCE OF THE METHOD OF MANUFACTURE.

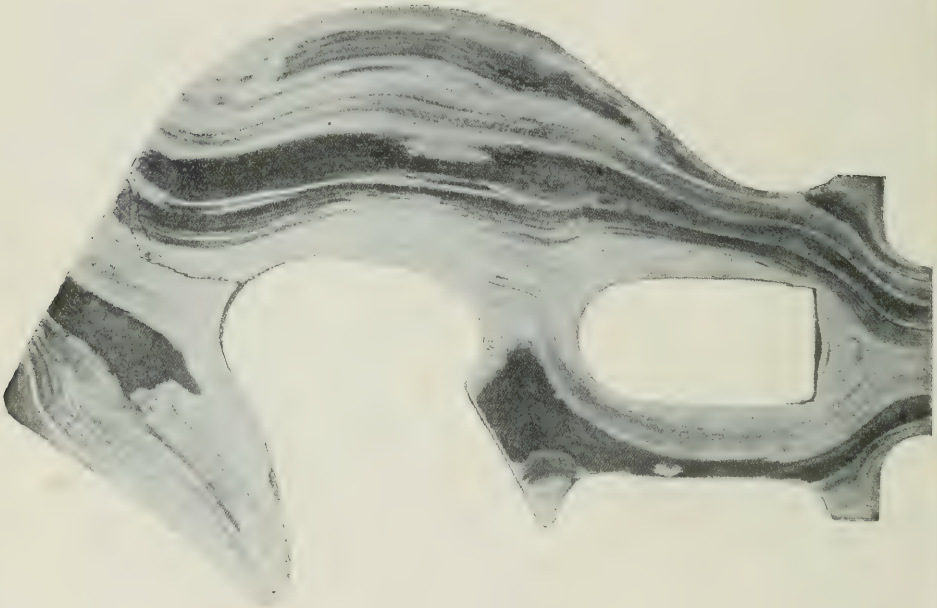


Fig. 550.—Influence of the method of manufacture.

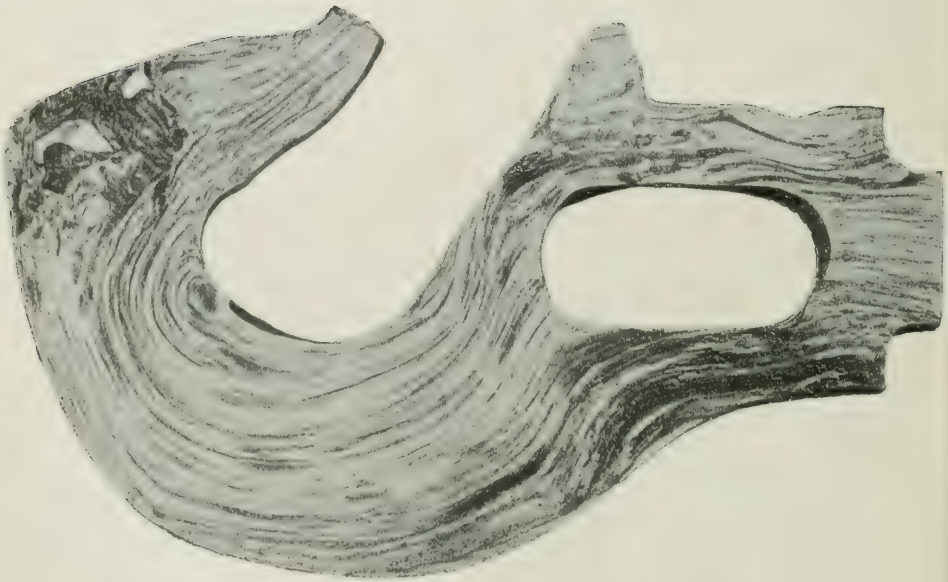


Fig. 549.—Influence of the method of manufacture.

ETCHING TESTS—INFLUENCE OF THE METHOD OF MANUFACTURE.

FIG. 551.—Chain link.
Etchant: Iodine solution.

FIG. 552.—Portion of an automobile connecting-rod.
Etchant: Iodine solution.

FIG. 553.—End of automobile carden shaft. Slow etching.

ETCHING TEST—INFLUENCE OF THE METHOD OF MANUFACTURE AND HETEROGENEOUS COMPOSITION.

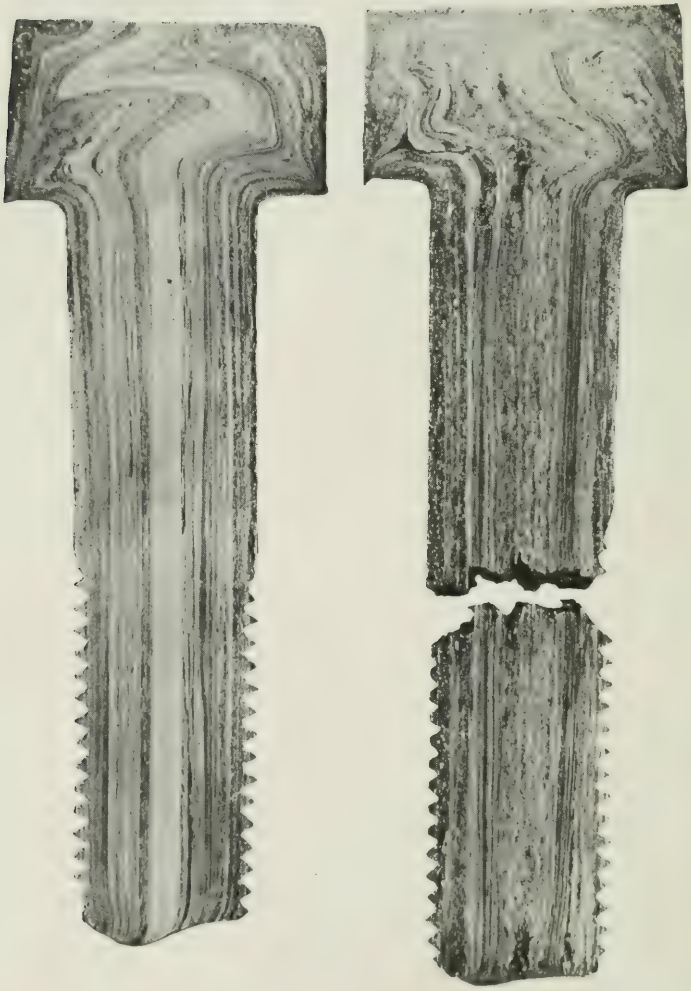


Fig. 554.—Steel bolts, fractured whilst in use owing to segregation, slag, large crystalline structure and method of manufacture.

Etchant: Prolonged etching with picric acid.

have been investigated and explained by Frémont as the result of the presence of such segregation (Fig. 541, Pl. CVII.).

The liquation in cast alloys may be similarly observed in the case of copper alloys. The illustration (Fig. 517, Pl. XCVIII., p. 262) shows the cross section of a bronze bearing containing lead; after polishing the lead appears as isolated particles.

2. **Application to Chemical and Mechanical Tests.**—The etching test gives a clear indication of the chemical heterogeneity of the material but does not enable a quantitative determination of the composition or properties to be obtained, it merely outlines the heterogeneous area, which should then be subjected to the necessary chemical and mechanical tests.

(1) *Chemical Analysis.*—Any systematic analytical examination should be preceded by an etching test; that is, for any given section, the sample for analysis should be chosen after the macrographic examination. Failure to obtain a representative sample is one of the most frequent causes of not obtaining concordant results from analyses. If the average or mean analysis is required it is preferable to obtain the sample from the whole surface by sawing or planing instead of taking drillings from various points.

If the material is to be examined microscopically as well as chemically, the samples should be taken from the same area, the macrographic structure serving as a guide in their selection.

(2) *Mechanical Tests.*—The results obtained from the etching tests should be verified by impact tests on notched bars (Heyn, Frémont). The examination of small impact test pieces obtained from different areas show considerable differences in mechanical properties due to chemical heterogeneity.

3. **Examination of Various Processes of Manufacture (soldering, brazing, welding, cementation).**—The etching test will show whether the material has been welded and also whether the materials joined together in this manner are of different composition. Examples are shown in Figs. 546–548, Pl. CX.

Also with case-hardened material the thickness of the case may be easily seen in a section of the metal (unquenched) after simple polishing and etching in picric acid. An examination by concentrated oblique light reveals the pure pearlite areas, the brilliant cementite needles and the clear unetched grains of ferrite; therefore it is even possible to form an estimation of the distribution of carbon in the cemented zone.

4. **Examination of the Internal Method of Deformation during the Mechanical Treatment of the Metal.**—By examining material which is distinctly heterogeneous, such as welding iron, the etching test may be used as an indirect method of examining the successive stages of deformation.

The different results obtained by hand and machine riveting may be shown in this manner, by etching tests on longitudinal sections. In a similar manner, Frémont has shown that the deformation and fracture produced by stamping and shearing are due to tensile stresses and not shearing stresses as previously supposed. Fig. 543, Pl. CIX., illustrates the effects produced at successive stages in the stamping of flat sheet iron, in which etching tests have been carried out on sections cut through the axes of the holes after stamping. The results obtained from such tests have caused Frémont to consider the relation between the shearing stress and ultimate tensile stress for any material; the results are proportional in the case of ordinary structural steel.

5. **Examination of the Method of Forging or Manufacture.**—This examination is the inverse of that described above; the method of deformation is to be investigated and the final result affords the only data obtainable.

(*a*) With extremely heterogeneous material—puddled iron, wrought iron, welding iron—the etching test will show the arrangement of the flow lines very clearly and the method of forging may be readily deduced; therefore this test may be used as a method of control or examination when any definite process of forging is required. Figs. 549, 550, Pl. CXI., illustrate tests carried out on railway coupling links. The link shown in Fig. 550 had fractured whilst in use; the hook, instead of being forged according to the specification, had been cut and bent out from the material forming the body of the link.

Fig. 551, Pl. CXII., illustrates a chain link, Figs. 544, 545, Pl. CIX., hot flattened rivets, Fig. 554, Pl. XCIII., steel bolts, Figs. 552, 553, Pl. CXII., automobile parts, Figs. 559, 560, Pl. CXVI., sections of automobile connecting-rods, Figs. 561, 562, Pl. CXVII., shell bases, clearly showing the methods of manufacture and the effects produced.

(*b*) With homogeneous steels, the examination of the macrostructure at low magnifications by means of a hand magnifying glass enables information of a similar nature to be obtained from the distribution and arrangement of the flow lines of the metal. Figs. 552, 553 illustrate sections of automobile parts.

By similar tests, of longitudinal sections, it is possible to discover whether an automobile crankshaft has been forged or merely machined to shape, the latter being an unsatisfactory method of manufacture. Further examples may be found in the previously quoted paper by Cloup.

6. **Quenched Articles.**—A brief account of the examination of quenched articles must now be given to render this description complete. Quenched sections are rarely examined owing to the difficulties encountered in obtaining such sections in an unaltered

EFFECT OF HEAT TREATMENT.

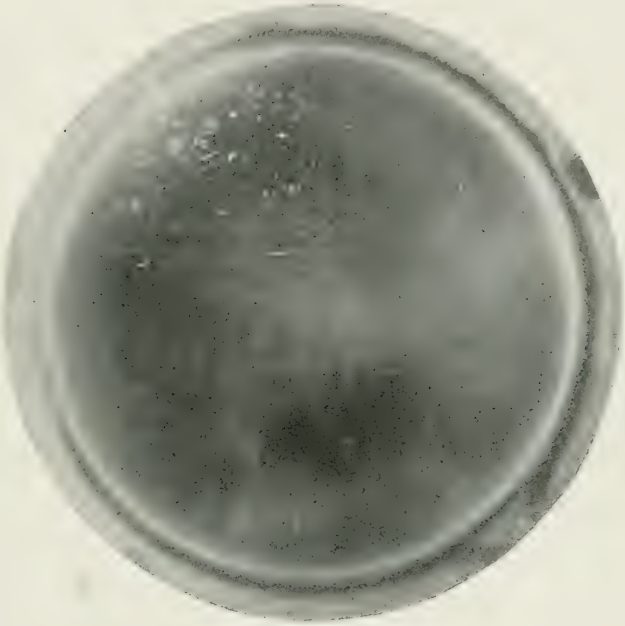


Fig. 555.—Transverse section of a case-hardened steel bar.

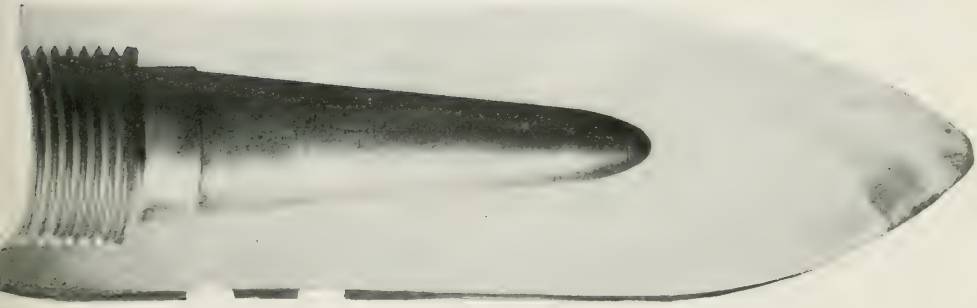


Fig. 556.—Longitudinal section of a steel shell that has been heat treated and fired.

SULPHUR PRINTS ON BROMIDE PAPER—SEGREGATION.

Fig. 557.—Segregation in a medium carbon steel showing the distribution of sulphur.

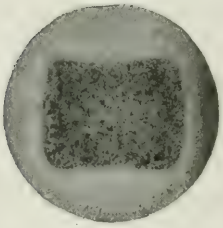
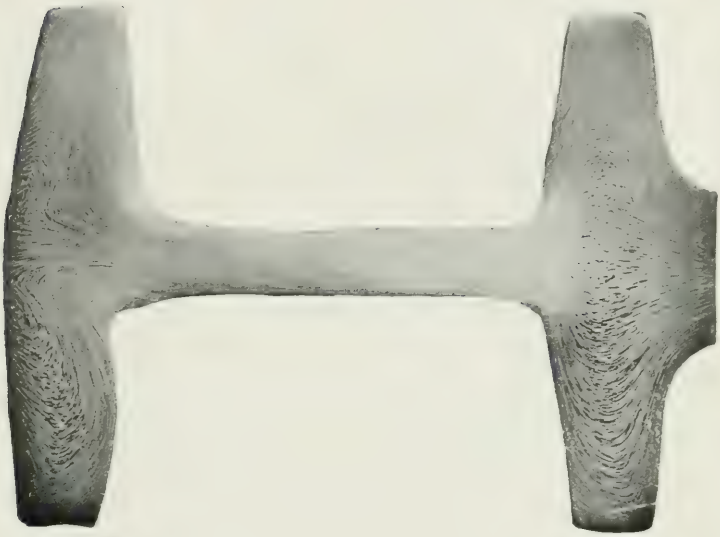
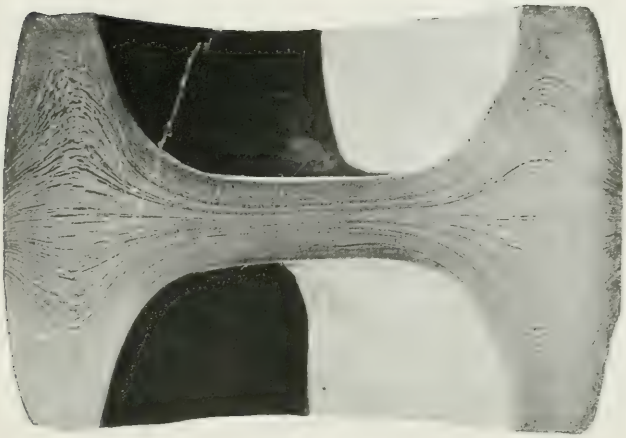


Fig. 558.—Segregation in a medium carbon round steel bar. The dark sulphide area is clearly shown.

MACROSTRUCTURE OF FORGED STEEL.

Etchant: Stead-Le Chatelier reagent.

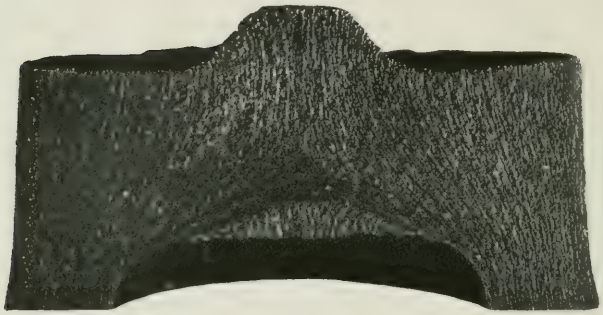


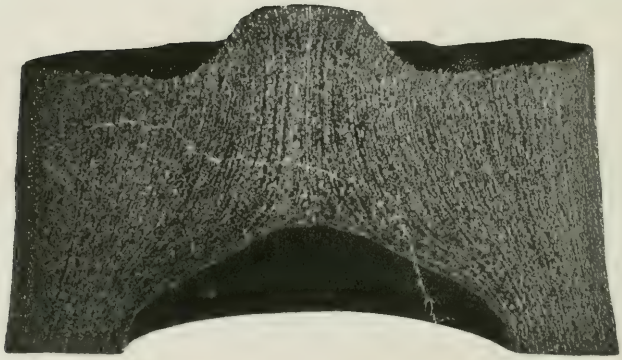


FIGS. 559–560.—Sections of automobile connecting-rods.
Stamped medium carbon steel.

MACROSTRUCTURE OF FORGED STEELS (*cont.*).

Etchant : Dilute sulphuric acid, 20 % H_2SO_4 at 80° C.





FIGS. 561-562.—Forged 75 mm. shell bases.
Stamped by two different methods.

condition, for the operation can only be performed by a skilled operator, and the method of cooling the surface during preparation must be extremely efficient (water sprays, etc.); moreover, the preparation of large sections of this nature becomes very expensive.

Polishing and etching, as for microscopical examination, reveal, in the case of a chemically homogeneous quenched steel, a heterogeneity due to quenching which may be observed even with small sections showing dark patches or lines, and indicating the troostite areas. Therefore, in every case, it is advisable to examine the general outline of the macrostructure before proceeding to the microstructure; for by this means the effects produced by the particular method of quenching are clearly revealed—agitation of the bath, contact of the articles with one another or with the containing vessel, support, tongs, etc., which are used to support or agitate the articles during quenching.

Tempering causes the coloration produced by the etching reagent to be uniform, while local tempering is shown by darker coloration on etching; but, as a general rule, the most severely quenched sections (martensite) are the least affected (coloured) on etching. Further information, however, will be found in the description of the constituents of quenched steels.

Fig. 556, Pl. CXIV., illustrates the section of a shell after firing; the portion least attacked on etching is the surface where quenching produces its greatest effect, but several local areas will be seen to be more coloured.[1]

1. At the point of the shell tempering has occurred owing to the heat generated by impact.

2. Lines across the surface, which are also tempered sections of the material caused, either during the sectioning of the shell by an unequal action of the grinding wheel, or, more probably, by a momentary overheating due to the absence of cooling water.

In the case-hardened quenched specimen (Fig. 555, Pl. CXIV.), the phenomenon is more complex, as there is a simultaneous reduction in the carbon content and rate of cooling on passing from the periphery to the centre of the section; but the general result is a dark annular ring, situated a small distance below the surface, indicating troostite and the lighter surface of martensite.[2] The nearer the dark annular ring approaches the surface, the more rapid the decrease in hardness in depth.

[1] This is explained by the differential coloration of the constituents of quenched steels as shown by the macroscopic examination of these constituents (Pl. XL., Fig. 241).

[2] This illustration should be compared microscopically with Fig. 315, P. XL., illustrating the edge of a case-hardened and quenched gear-wheel.

CHAPTER VIII

SUMMARY

THIS last chapter will be confined to a short summary of the information that may be obtained from a metallographic examination, and will include a brief account of the various industrial alloys considered in the previous chapters.

GENERAL RESULTS

1. **Examination of a Polished Section Unetched.**—(*a*) *Appearance of Physical Defects.*—Gaseous inclusions: blow holes, cavities, cracks (frequently cavities are produced by the removal of some inclusion during polishing or etching, *e.g.* graphite in cast iron).

Solid inclusions: oxides (Cu_2O in Cu, SnO_2 in bronzes), sulphides (MnS in steels), slag, graphite in cast irons, nickel and certain alloys of this metal.

(*b*) *Information as to the Constitution of the Alloy.*—Polishing leaves the harder constituents in relief (bas-relief polishing); cementite and carbides in ordinary and special steels, hard constituents (SbSn, Cu_3Sn) in bearing metals. Prolonged polishing causes coloration or differentiation in the appearance of certain constituents: the δ constituent in bronzes, β in brasses, γ in aluminium bronzes.

(*c*) *Information as to the Chemical Composition.*—The presence of lead particles in copper alloys, graphite in cast iron.

2. **Examination of a Polished Section after Etching.**—(A) *Alloys containing only One Constituent.*—(*a*) Information as to the chemical heterogeneity which disappears on annealing: α solid solution in bronzes, brasses, aluminium bronzes; solid solutions in cupro-nickels, copper-nickel-zinc alloys, etc.

(*b*) Information as to the mechanical and thermal treatment to which the alloy has been subjected, the size of the polyhedral structure being dependent on such treatment: annealed copper, α brasses, cupro-nickels, etc.

(*c*) Effects produced by local mechanical treatment causing heterogeneity: local cold-work and annealing after local cold-work.

(*d*) Indications of heat treatment which may be deduced from

the presence of certain unstable or transitional constituents: martensite and osmondite in steels, martensitic structure in certain other alloys affected by quenching.

(*e*) Information as to the mechanical properties of the material which may be deduced from certain characteristic structures: martensite in ordinary steels, aluminium bronzes, etc., which corresponds to an increase in hardness and tensile strength of the material as compared with the annealed metal; martensite in annealed special steels, suggesting a high ultimate strength combined with great hardness; the polyhedral structure in special steels, indicating a high impact figure, while the brittleness of all alloys consisting of a single phase is dependent on the size of the crystal grains (cold-worked metal, overheated metal, alloys with other metals in solid solution).

Metallographic examination affords no information as to the chemical composition of an alloy consisting of one constituent, except in special instances. Thus, the presence of martensite in annealed steels indicates the presence of Ni, Mn, or Cr.

(B) *Alloys consisting of Two Constituents.*—(*a*) Information as to the chemical composition may be obtained from the completely annealed material by estimating the proportions of the two constituents present; *e.g.* carbon steels, copper-tin alloys $\alpha+\delta$, copper zinc alloys $\alpha+\beta$, aluminium-bronzes $\alpha+\gamma$.

(*b*) Information as to the thermal and mechanical treatment from the size and distribution of the constituents: thus, prolonged annealing causes coalescence—the formation of banded pearlite in rolled steels—and there is extremely fine division of the constituents in material subjected to severe cold-working (brass pins).

(*c*) Indications of previous heat treatment, owing to the simultaneous existence of one constituent in equilibrium and one unstable constituent or two constituents not in equilibrium. Examples:—

1st Case: Ferrite and martensite in quenched steels of low carbon content.

2nd Case: Martensite and austenite in quenched steels of high carbon content, or martensite and osmondite in quenched or quenched and tempered steels.

(*d*) In conformity with the above, heterogeneity due to local thermal or mechanical treatment. Variations in structure on passing from the surface to the interior of quenched steel specimens; also, variations in the size of the constituents, owing to the effects produced by local cold-work.

(*e*) Information as to the mechanical properties of the material which may be deduced from certain characteristic structures, or, in other words, the distribution of the two constituents. Examples:—

Widmanstaetten structure in steels.

Granular pearlite in steels.

Apparent content of brasses and bronzes.

Banded structure of forged and rolled alloys (variations in properties in the two directions).

(*f*) Information as to the chemical treatment to which the material has been subjected: variations in the proportions of the constituents, formation of new constituents. Examples:—

1st Case: Cementation of ordinary carbon steel; manfacture of malleable cast iron.

2nd Case: Cementation of special steels (cementation of a pearlitic nickel steel and the formation of martensite); galvanising and the formation of an iron-zinc alloy.

(*g*) Information as to the method of manufacture: puddled iron, the presence of slag being characteristic, cast alloys possessing a dendritic structure, autogeneous welding and brazing, etc.

(*h*) Information as to the imperfections caused by faulty manufacture.

Liquation, local carbonisation or decarbonisation caused during the heating of steel, dezincification of brass, overheating of the material, etc.

(*i*) Indication of impurities contained in the metal: appearance of a special constituent in an alloy which, normally, consists of a single constituent: bismuth and antimony in copper and α bronzes, lead in zinc, α bronzes, α brasses, etc.

(C) *Alloys consisting of more than Two Constituents.*—The information to be obtained is similar to that described for alloys containing two constituents.

The following case may be mentioned as being of considerable industrial importance: Appearance of a special constituent in an alloy consisting normally of two constituents; phosphide of iron and sulphide of manganese in cast iron, phosphide of copper in bronzes, Cu_3Sn in brasses containing tin.

Special Note.—As a general rule the microscopical aspect or structure is dependent on factors of two classes: chemical composition and treatment; therefore, in most cases the examination of two separate specimens is *essential*, the one in the cast condition or as received, the other in the completely annealed state.

DETAILED CLASSIFICATION OF DATA OR INFORMATION TO BE DEDUCED FROM THE MICROSCOPICAL EXAMINATION OF VARIOUS CLASSES OF ALLOYS

Irons.—Presence of slag. Size of grain. Discoloration of ferrite after etching, owing to the presence of impurities. Existence of Neumann's lines and their relation to brittleness.

Steels.—Presence of slag. Size of grain. Estimation of carbon content (amount of pearlite in the completely annealed material).

Mechanical Treatment.—(Widmanstaetten structure indicating brittleness, cellular structure indicating normal treatment, banded distribution of the pearlite, indicating different mechanical properties in different directions), indications of local cold-work.

Thermal Treatment.—Quenching (martensite of varying fineness, osmondite, ferrite, and cementite present in varying quantity), annealing (distribution of the constituents, granular pearlite and cementite, large grains), presence of free cementite in the pearlite or coarse pearlite in overheated steels. Chemical treatment: cementation (distribution of the pearlite and cementite before quenching), malleable cast iron (decarburisation).

Cast Iron.—Classification of the cast iron (presence of graphite and phosphide of iron), manganese sulphide inclusions. Estimation of the free cementite and the pearlite.

Special Steels.—Determination of the characteristic structure (pearlite, martensite, polyhedral structure, complex carbides). Corresponding deductions as to the mechanical and physical properties of the metal. Heat and mechanical treatments. Chemical treatment: cementation. Grain size (polyhedral structure).

Copper and Copper Alloys.—Presence of, oxide of copper, lead, arsenic, bismuth, antimony in copper; oxide of tin, arsenic, and antimony in bronzes. Estimation of the quantity of arsenic in copper.

Estimation of tin in the $\alpha+\delta$ bronzes, of zinc in the $\alpha+\beta$ brasses, of aluminium in the $\alpha+\gamma$ aluminium bronzes. Estimation of lead. Determination of the apparent content of the special copper alloys. Information as to the mechanical treatment and properties of the metal.

Mechanical Treatment.—Determination of the method of manufacture (cast, forged, rolled, drawn, pressed, etc.); estimation of the amount of cold-work, local cold-work, amount of annealing in the case of copper, brasses, bronzes, cupro-nickels, and nickel silvers.

Heat Treatment.—Quenching, characterised by a martensitic structure, especially in the case of aluminium bronzes; in the annealed state, the equilibrium structure.

Bearing Metals.—Presence of a hard constituent, the quantity depending on the conditions of employment. Presence of compounds of copper and tin (Cu_3Sn), antimony and tin (SbSn), of lead, etc.

It may be stated that the general statements relating to heat and mechanical treatments, and the method of manufacture, are directly applicable in this instance.

The above summary is a brief outline of many of the industrial applications of microscopic and macrographic examinations.

Like other methods of examination, it does not offer a complete solution of all the difficulties to be met with in the manufacture and the use of the various alloys, but in many instances it verifies, completes, and explains the information obtained by other methods of investigation. If in some instances such an examination yields no useful results, in others the information thus available is to be obtained by no other method.

INDEX

NOTE.—The principal references are shown in heavy type in cases of two or more references under one heading.

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